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Recovery of silica gel in the adsorption purification of zirconium

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NOTE TO USERS

RECOVERY OF SILICA GEL IN THE ADSORPTION PURIFICATION OF ZIRCONIUM

by

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GLOSSARY OF SYMBOLS

Hf/Zr x 100	the weight ratio of hafnium to zirconium (multiplied by 100) in a mixture of the oxides, as reported from spectrographic analysis of the oxide sample. See also R.
K_o	the hafnium separation factor, ratio R_G/R_F, for an adsorption system attained at equilibrium between feed and silica gel.
P	the quantity of product solution from an adsorption operation, in gallons. More specifically refers to the amount of specification product from a given time interval of continuous operation.
R	(subscripted with F, P, or G), the concentration of hafnium in feed, product, or on the gel, respectively, expressed as the weight ratio Hf/Zr x 100. With low hafnium concentrations may also mean percent hafnium, where percent hafnium and Hf/Zr x 100 are practically equivalent.
S_H	the hafnium adsorption factor, factor by which the hafnium is reduced from feed to product by adsorption on gel, equal to the ratio $x_P R_P v_F / x_P R_P v_P$.
v	(subscripted with F or P), the volume of feed or product solution, respectively, referred to a batch adsorption test to determine S_H. Expressed as milliliters per gram of gel.
W	the quantity of silica gel used in an adsorption operation, in pounds. More specifically refers to the amount of gel used in a given time interval in a continuous adsorption to produce a given amount of specification product P.
$\frac{W}{P}$	the ratio of the pounds of gel used per gallon of product in a continuous adsorption operation.
x	(subscripted with F or P) the total concentration of solute in feed or product, respectively. Expressed as grams of oxide per milliliter of solution.

ΔH_w heat of wetting of silica gel. Expressed as calories per gram of gel, wet basis.

% (symbol for percent), the specific analysis of a given material; for example, a feed containing 2.5% hafnium by weight. The word "percent" designated a change or error; for example, a 2.5 percent error in material balance.

I. SUMMARY

An investigation was made to determine the conditions under which silica gel adsorbent could be regenerated for re-use in a process for purifying zirconium. The purification process was based on preferential adsorption of the impurity hafnium by silica gel. When the gel had lost its adsorptive power, regeneration was desirable to reduce the amount of new gel required, and so to reduce the cost of the process.

Treatment of the silica gel to be reclaimed was first studied on a small scale to determine approximately the quantities of reagents required for regeneration, and the conditions for the treatment. Laboratory experiments also were made to compare the purifying capacity of regenerated gel with that of fresh gel.

The gel reclamation process proposed consisted of these steps: First, the occluded hafnium-zirconium feed solution was drained off the gel as thoroughly as possible, and an agitated batch washing with methanol served to remove mechanically occluded solution. Second, the washed gel was treated with aqueous sulfuric acid, which stripped the adsorbed materials from the gel. Third, the acid strip was drained off as thoroughly as possible, and the gel was thoroughly water-washed. Finally, the washed gel

was activated by heating to restore its adsorptive capacity.

It was found that unstripped adsorbate left on the gel, and improper activation, were the primary factors causing the gel to lose capacity for adsorbing hafnium. Pilot plant stripping treatments showed that gel could be satisfactorily stripped and re-activated three times, with residual material on the gel kept very low by use of a nominal quantity of strip solution. At the end of three cycles of use the hafnium adsorptive capacity of regenerated gel compared favorably with that for fresh gel.

Evaluation of regenerated gel in a large-scale adsorption operation could best be made by determining its residual material, heat of wetting, and moisture content. The residual oxide analysis would provide a control on the stripping operation, while the heat of wetting and moisture content would show whether or not the gel had been properly activated.

In the stripping treatment, zirconium adsorbed along with hafnium in the purification was effectively lost because zirconium could not be readily reclaimed from the strip solution. This zirconium loss was calculated to be about 13 to 18 percent.

The cost of gel reclamation was found to be about $0.05 per pound of gel, compared to $0.44 per pound for

new gel. The major reduction in the cost of zirconium purification through gel recovery was in the first three or four re-uses, beyond which gel recovery would not materially influence the cost of zirconium.

An estimation for a semi-works plant producing 1000 pounds of zirconium per month by the adsorption process showed the overall cost to be $7.10 per pound of zirconium, including gel reclamation. In comparison, the overall cost established by actual operation of the Y-12 solvent extraction process was shown to be $5.37, or less. Thus the adsorption process for purifying zirconium proved somewhat more expensive than the solvent extraction process, even with gel recovery.

II. INTRODUCTION

The use of zirconium as a structural material in nuclear reactors depends upon it being essentially free of hafnium, because hafnium has a high cross-section for neutron capture. Hafnium invariably occurs with zirconium in nature, and its removal is complicated by its close chemical similarity to zirconium.

Prior to the emergence of the atomic energy program, the development of methods for separating zirconium and hafnium were quite limited, there being relatively few uses for either metal in pure form. At the Ames Laboratory, investigations were made toward development of a zirconium purification process suitable for large scale production. Dr. R. S. Hansen and his associates (8) at the Ames Laboratory found that high-grade silica gel preferentially adsorbed hafnium from a methanol solution of hafnium-zirconium tetrachlorides.

The silica gel used in the adsorption was activated by dehydrating to about 3.5% moisture, by heating at 300°C. and was then cooled and placed in a Pyrex glass column partly filled with methanol (to aid settling the gel into a bed). The methanol solution of hafnium-zirconium tetrachlorides was passed upward through the gel bed, and after having displaced the methanol used in

loading the column with gel, the effluent solution was collected as product. This solution was evaporated to recover the methanol, the zirconium remaining as a water-soluble residue from which purified zirconyl chloride octahydrate could be obtained by crystallization. By this procedure the hafnium content of the zirconium could be reduced from about 2% to about 0.01%.

The process as developed by Hansen involved a batch-wise operation, because the bed of silica gel would purify only a limited quantity of feed solution. The gel then became loaded or "spent" to the extent that undesirable quantities of hafnium would pass through unadsorbed, the column had to be shut down, and the silica gel removed and replaced with fresh gel. R. H. Giffen (7) demonstrated that the process could be adapted to continuous countercurrent operation, and developed a pilot plant design and cost estimate showing the process might be made competitive with other methods of zirconium purification.

Since the silica gel constituted an important cost item in the adsorption process, recovery of the spent gel warranted further investigation. Reclaimed gel comparing favorably with the fresh gel might be reused several times before discarding it. This work was undertaken to study processing of the spent gel, to reclaim gel with a high adsorptive capacity as cheaply as possible. Also, the

evaluation of the useful life of the gel, and factors causing the gel to lose activity, were studied. Determination of gel quality by relatively simple tests was of interest as a means of controlling the quality of the reclaimed gel.

III. REVIEW OF THE LITERATURE

Prior to the work by Hansen and his associates, virtually all the experimental study devoted to silica gel dealt with adsorption of liquids and condensable vapors, and their properties in the adsorbed state. Relatively little of this work bears directly upon the present process or its problems, but that which pertains to fundamental properties of silica gel might appropriately be reviewed. From the standpoint of understanding the nature of the recovery problem, it is well to discuss the nature of silica gel.

In 1911 Zsigmondy (17) postulated the structure of silica gel to be a system of fine capillary tubes of variable diameter. He noted the lowered vapor pressure of water adsorbed on the gel, and attributed this lowering to the normal laws of capillarity. In 1925 Fells and Firth (5) established definitely that silica gel consists essentially of the system SiO_2-H_2O, the silica being an intricate network of capillary and micro-capillary tubes which give the gel a very high specific surface area.

Bartell and Almy (2) in 1932 proved that the water present in silica gel is of two types. First, the "capillary" or adsorbed water is bonded by the adsorptive or surface forces possessed by the gel. The other type of

water is the "bound" water which is bonded to the silica chemically, and is an intimate part of the gel structure. Removal of this bound water causes permanent loss of gel surface and therefore loss of adsorptive activity, probably as a result of the collapse of the capillary walls due to decomposition of the SiO_2-H_2O compound.

Ewing and Bauer (4) developed a calorimetric method for establishing the heat of wetting associated with adsorption of water by the gel. They correlated this heat of wetting with the total moisture content of the gel, and found a maximum heat of wetting (32 calories per gram of gel) occurred with 4.0% moisture on the gel. With either greater or smaller total moisture content on the gel, the heat of wetting was less than the maximum of 32 calories per gram of gel. The lowered heat of wetting with gel having more than 4% moisture was ascribed to the adsorbed water occupying gel surface area. The lowered heat of wetting with gel having less than 4% moisture was explained as a sintering of the gel, breaking down the gel surface by decomposition of the SiO_2-H_2O compound.

Ewing and Bauer thus associated the optimum 4% moisture with the point at which the water was (theoretically) all bound as SiO_2-H_2O. With a greater total moisture content, some of the gel surface was made unavailable by being blocked with adsorbed water. The

adsorbed water could be removed by heating the gel at about 300°C to activate the gel, or make available, the surface area that had been occupied by the adsorbed water. So long as the gel was not overheated, its total moisture would not change appreciably from the 4% optimum, the heat of wetting would remain a maximum, and the gel could be used many times. Heating the gel appreciably over 300°C would cause a decrease in moisture content from 4%. i.e, a loss of bound moisture, and a permanent loss of gel activity due to sintering the gel surface.

The surface area of silica gel was determined by Ewing and Bauer, and was estimated to be 1×10^6 square centimeters per gram of gel. Felsing and Ashby (6) found the surface to be 2.7×10^6 square centimeters per gram by adsorption of ammonia. Rao (16) found it to be 7×10^6 square centimeters per gram by adsorption of water. Hansen (9) used gas adsorption to determine surface area of the gel which was used throughout this investigation. Hansen estimated the area to be 7×10^6 square centimeters per gram of gel.

Hansen stated in his original work on the adsorption process (9) what he considered to be optimum conditions for the process. The feed solution was specified at 20% to 23% by weight zirconium-hafnium tetrachloride dissolved in anhydrous methanol. Higher concentrations than

this gave undesirably viscous solutions, while lower concentrations were uneconomical from the standpoint of requiring more methanol and larger equipment.

The feed solution was found to be quite hygroscopic, and was kept out of contact with air to avoid picking up moisture. The reaction between moisture and the solution was found to be essentially a hydrolysis between the methanol and tetrachlorides, producing gaseous methyl chloride and hydrogen chloride. The effect of the hydrolysis on the adsorption in purifying zirconium was not entirely clear, but investigations did show that water entering the feed solution caused poor adsorption results (12).

Hansen demonstrated that gel of conventional or commercial grade, i.e., about 5% moisture, which gives very satisfactory results in air-drying and similar applications, did not give very good results in the zirconium purification process. He recommended activation of the gel to give a moisture content near the optimum of 4% found by Ewing and Bauer. Gel with a moisture content of 3.5% to 4% was found to give much better results in the zirconium purification than the gel having 5% moisture. J. L. Baer (1) subsequently showed that, for pilot plant quantities, tray drying for 24 hours at 275°C in a gas-fired oven gave satisfactory results.

Hansen's 1950 summary report (8) indicated the steps in a suitable treatment of the spent gel. The gel coming from the adsorption column has considerable solution occluded, much of which can be removed readily by simply draining and aspirating. In addition, some occluded material is readily removed by washing the drained gel with pure methanol. The methanol wash recovers some zirconium in a form in which it may be recycled (as feed solution) in the adsorption purification process. This methanol-washed zirconium would otherwise be lost in the sulfuric acid strip solution which Hansen recommended to follow, to remove all adsorbed hafnium and zirconium from the gel.

Hansen found that acid desorbs, or strips, adsorbate from the gel. He recommended that a 2N HCl-methanol solution might be used first, as this solution was found to remove zirconium preferential to hafnium. This strip would serve to enhance the zirconium recovery, because the low-hafnium solution could be neutralized with anhydrous ammonia and recycled (as feed solution) in the adsorption purification process. The stripping with 7N aqueous sulfuric acid solution would then follow the HCl-methanol stripping. The sulfuric acid was found to remove the remaining adsorbate. A thorough washing with pure water removed the acid, after which the gel could be reactivated to the desired moisture content for reuse.

One of the shortcomings inherent to the adsorption process was that a purification of hafnium was not obtained due to the considerable amount of zirconium adsorbed on the gel with the hafnium. The methanol washing served to reduce zirconium occluded on the gel, and the HCl-methanol solution actually stripped some of the zirconium adsorbed, but considerable zirconium could not be removed except by the final strip with sulfuric acid. The adsorbate removed by the sulfuric acid was found to analyze generally from 15% to 25% hafnium by weight. Preparation of high-hafnium fractions was studied by Jacobs (10). He was able to obtain high-hafnium concentrates by converting the final stripped fractions, which he obtained as oxides, back to tetrachlorides and repeat the adsorption and stripping cycles. Repeating the adsorption and stripping over two or three cycles enabled a hafnium enrichment to about 90% hafnium to be attained.

Jacob's processing of the sulfuric acid strip involved precipitation of the solute as hydroxide by neutralizing the strip with ammonia. The hydroxide was converted to oxide by calcining at about 500°C, and the oxide then had to be converted to tetrachloride by a vapor-phase chlorination with carbon tetrachloride in a special apparatus. It is thus clear that adsorbates obtained from the sulfuric acid strip could not be readily purified to

obtain either zirconium or hafnium. Any zirconium left on the gel, i.e., not removed by the methanol wash or methanol strip, would thus be lost in the sulfuric acid strip. Treatment of the sulfuric acid strip to reclaim zirconium and hafnium is so involved that it cannot be considered a part of gel recovery.

Investigation of the adsorption rate in the zirconium purification was made by Baer (1). The primary purpose of this study was to determine the importance of the time element in the adsorption, i.e., whether the hafnium adsorption was extremely slow or quite rapid. It was also desired to determine the adsorptive capacity of the gel. Baer prepared batchwise contacts between activated gel and feed solution. The feed solution was of about the same composition as that used by Hansen, i.e., 20% tetrachlorides in methanol, the solute being about 2% hafnium. The contact time allowed for the adsorption was varied from 0.1 to 1000 hours, and it was shown that at least 120 hours were required to permit a satisfactory approach to equilibrium between the gel and solution phases. The evaluation of equilibrium and its approximation in time were desired to enable evaluation of subsequent work without having to refer to true equilibrium.

Baer evaluated the distribution of the components, hafnium and zirconium, as the quotient of the hafnium

concentration of the material on the gel to the hafnium concentration of the material in the effluent (product) solution. Hafnium concentration was obtained by spectrographic analysis of the oxide obtained in each case, and was reported as the weight ratio Hf/Zr x 100 (see Appendix B). The quotient calculated by Baer, which he designated as K, corresponds to a hafnium distribution coefficient which will vary directly with the degree of separation obtained between hafnium and zirconium. He found that K was a constant at equilibrium, with a value of near 15.

Giffen (7) developed a correlation for the several variables involved in the adsorption system, obtaining linear form expressions for the distribution of each of the components, hafnium and zirconium. These expressions were then used to correlate data calculated from Baer's equilibrium measurements and obtain the relations necessary for any desired scale-up of the adsorption process. Several pilot plant continuous column adsorption runs were made which served to give data corroborating Giffen's relations among the scale-up factors. Giffen also applied statistical analysis to Baer's data to obtain what he considered a more reliable value of the distribution coefficient K. Giffen termed this a separation factor, symbol K_0, and found the value by statistical analysis to be 13.18.

A plant design and cost analysis was prepared by Beyer and Giffen (3) for a semi-works plant producing 1000 pounds of zirconium per month. The cost of zirconium purification was found to be $7.60 per pound of zirconium (as purified $ZrOCl_2.8H_2O$) compared to $10.14 per pound as ZrO_2 for the Oak Ridge Y-12 process. More recent work on the Y-12 process has been reported by Ramsey and Whitson (14, 15) indicating that the cost of the process has since been lowered to $5.37 per pound of zirconium (as purified ZrO_2).

The essential point in Giffen's correlation for the plant design was that the quantity of gel to be used in the purification was decided arbitrarily, and this fixed the column design for the zirconium purification required. The quantity of gel was specified as W/P, W being the pounds of activated gel required for P gallons of product solution obtained, for a given period of steady-state column operation. Stoichiometric relations showed that a minimum W/P of 1.19 pounds of gel was required per gallon of solution, to obtain purification of the feed solution he assumed to be used. Feed solution properties were assumed to be the same as for the solution used by Hansen, with a product analyzing 100 parts per million of hafnium or less.

If a low value of W/P were chosen for a plant design, i.e., a value close to the calculated minimum, less gel would be consumed in the adsorption process and the zirconium yield would be relatively high, but column operation would be sensitized to small variations in the flow rates of solution and gel. On the other hand, a larger W/P would make column operation easier but would increase the amount of gel used and consequently decrease the zirconium yield. Giffen recommended a minimum W/P of 1.5 or 2.0 pounds of gel per gallon of solution for usual plant design, to strike a balance between ease of column operation and gel requirements, and still obtain a good zirconium yield (about 87 percent, according to Giffen's figures).

From Giffen's relationships for the separation factor K_0, he stated that the chemical nature of the gel should influence the adsorptive capacity directly, so that any regeneration process should return the gel to its original condition in order to obtain satisfactory adsorption results. A decrease in the adsorptive capacity of the gel would probably also cause some decrease in the adsorption rate, though this would be of less importance in the continuous adsorption column than the purification obtainable.

IV. INVESTIGATION

A. Examination of Adsorption and Stripping Data on Batch Columns

The development of a suitable process for treating and reclaiming the spent gel involved a thorough consideration of each step in the treatment proposed by Hansen, as well as consideration of other possible treatments.

Jacobs (10) performed several batch column adsorption and stripping runs in preparing high-hafnium concentrates by adsorption on silica gel. In each run, freshly activated silica gel was initially contacted with feed solution which was passed upward through the silica gel column. The feed solution he used contained about 20% zirconium-hafnium tetrachlorides dissolved in methanol, with about 2% or more hafnium in the solute. The product solution passed out the top of the gel column, and solution samples were taken at various intervals to determine hafnium concentration. The degree to which the gel was loaded with adsorbed oxides, and particularly the hafnium concentration of the adsorbate, varied somewhat from run to run due to variation in the quantity of feed solution used per pound of gel charged to the column.

Of the nine runs completed by Jacobs, the four with normal low-hafnium feed, made in the six-inch column containing approximately forty pounds of gel, are of interest

here. The other five runs were made in one-inch and two-inch columns on much smaller quantities of gel, using high-hafnium feed. The loaded gel was treated to remove the adsorbed hafnium-enriched material, this treatment being essentially that proposed by Hansen for recovery of the spent gel. When the flow of feed solution was stopped the loaded gel in the column was treated as follows:

1. The occluded solution was thoroughly drained off.
2. The gel was washed with pure methanol (in some of the runs).
3. The gel was stripped with anhydrous HCl-methanol solution, which removed low-hafnium material from the gel.
4. The gel was stripped with 7N aqueous sulfuric acid, which removed all remaining adsorbate.
5. The stripped gel was washed with pure water.

The main purpose of the first three steps was to remove as much low-hafnium material as possible, so as to concentrate the hafnium on the gel. The sulfuric acid strip solution removed the hafnium and remaining zirconium, and thus served to regenerate the gel. The water-washing removed the occluded acid solution after most of the solution had been drained off the gel. The water-washed gel would then be ready for reactivation to the desired moisture content.

The four six-inch column runs provide data from a scale of operation that approximately corresponded to the scale that would be applied in gel treatment processing. From the data on these runs it was desired to analyze Jacob's gel treatment process by determining:

1. The amount of material washed from the spent gel with pure methanol, in comparison with the total amount of occluded and adsorbed material;
2. the stripping effect, if any, of pure methanol on the spent gel;
3. the amount of recyclable (low-hafnium) material stripped by the HCl-methanol solution, in comparison with the total amount of adsorbate.

Jacobs designated his six-inch column runs as 3, 4, 5 and 6. Runs 3 and 4 represented somewhat anomalous conditions for the purposes of this study, because the gel was not completely loaded with respect to hafnium, and the methanol washing was omitted. These runs are chiefly of value in comparing their total gel adsorbate content with the gel adsorbate content found in Runs 5 and 6 where the gel was methanol-washed. This matter will be discussed more fully in connection with the methanol washing.

Runs 5 and 6 are the most important from the standpoint of the gel treatment involved. In Run 5 the gel was completely saturated with respect to hafnium, sufficient

feed solution being passed through that the product had a final hafnium concentration equivalent to the hafnium concentration of the feed. The gel from this run would therefore correspond closely to gel that would be processed from normal zirconium purification operations. In Table 1 the data from Jacobs' runs are summarized, showing the material fed, methanol-washed, and stripped in each run. In Run 5 the material balance between feed and product-plus-stripped oxide is seen to check exactly. It should be noted that this balance includes column drainage with the feed, and methanol wash with the adsorption product.[1] The amount of material removed by methanol washing was established by reference to Jacobs' research notebook (11).

In Run 5 the methanol washing removed 624 grams of oxides from 37 pounds of gel. The oxide analyzed 2.5 in Hf/Zr x 100, the same as the final product obtained in the adsorption cycle. The feed solution analyzed 2.2 in Hf/Zr x 100, which may have been a low analysis since the product analyzed higher, or the latter may have been high. The total stripped oxide (adsorbate) weighed 1224 grams and analyzed 37 in Hf/Zr x 100. Items E1, E2, and F in Table 1 summarize the distribution of the total stripped

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[1] Personal communication from A. Jacobs, January 26, 1953.

Table 1. Adsorption and Stripping Data from Batch Columns.

	Jacobs' Run No.	3	4	5	6
A.	Gel condition at end of run	Hafnium-Unsaturated	Hafnium-Unsaturated	Hafnium-Saturated	Uniformly Loaded
B.	Silica gel used, lb.	37	40	37	40
C.	Total adsorption product, g. oxides	14,816	16,025	24,076	15,758
D.	Oxides removed by methanol wash, g.	no wash used	no wash used	624	1060 675
E.	Total HCl-methanol strip, g. oxides	863	972	727	896
	1. Recyclable g. oxides (percentage of total strip given)	380 (27.7)	650 (45.2)	none (0)	647 (54.7)
	2. Non-recyclable g. oxides (percentage of total strip given)	483 (34.6)	322 (22.4)	727 (59.4)	249 (21.1)
F.	Total sulfuric acid strip, g. oxides (percentage of total strip given)	521 (37.7)	465 (32.4)	497 (40.6)	285 (24.2)
G.	Total strip, E+ F, g. oxides (100 percent)	1384	1437	1224	1181
H.	Total occluded strip, D+E+F, g. oxides	1384	1437	1848	2916
I.	Stripped oxide content of gel, C/B, g. oxide per g. gel	0.0825	0.0792	0.0729	0.065
J.	Total product stripped oxide, C + G, g. oxide	16,200	17,462	25,300	16,939
K.	Total oxide fed, g.	16,200	17,500	25,300	16,940

Table 1. (Continued)

Jacobs' Run No.	3	4	5	6
L. Hafnium in adsorption product, g. oxide	76	125	179	161
M. Hafnium in HCl-methanol strip, g. oxide	51.75	31	51.57	35.55
N. Hafnium in sulfuric acid strip, g. oxide	195.9	194	247.45	157.45
P. Total hafnium, L+M+N, g. oxide	323.65	350	478.02	354.0
Q. Hf/Zr x 100 of feed	2.35	2.30	2.2	2.45
R. Hf/Zr x 100 of final adsorption product	2.20*	1.65	2.5*	1.30
S. Hf/Zr x 100 of overall adsorbate	24.9	25.9	37.0	22.3
T. Hf/Zr x 100 of methanol washing	no wash used	no wash used	2.5	1.4 2.7
U. Hf/Zr x 100 of recoverable material in HCl-methanol strip	2.18	2.11	none	2.39

*Probably high

oxide between the two strip solutions, the oxide removed by the HCl-methanol strip having been analyzed from Jacobs' data to determine the proportions of material that would be recyclable and non-recyclable. (These proportions are given in E1 and E2, respectively.) Material having a hafnium concentration equal to or less than the feed hafnium was considered recyclable. The analysis was made from Jacobs' composite hafnium analyses at various intervals of the continuous HCl-methanol stripping, which enabled ready calculation of the quantities having lower or higher hafnium concentration than the feed.

In Run 5 it was found that none of the material stripped by the acidified methanol was recyclable, since even the first material removed analyzed higher in hafnium than the original feed. Consequently the acidified methanol might well have been eliminated from the gel treatment, if gel recovery had been the primary object of this treatment. The sulfuric acid strip would have removed all the material remaining on the gel after the methanol washing, and the single stripping would have simplified the gel recovery process. The only advantage in using the acidified methanol in gel recovery would be the enriching effect on the hafnium stripped by the sulfuric acid and obtained possibly as a high-hafnium by-product of the gel treatment. The acidified methanol enriched

the hafnium to only a moderate degree, however, so the acidified methanol strip would contribute little to this process.

Run 6 was interesting because of the manner in which the loaded gel was obtained and treated. The gel was first uniformly loaded by contacting it with three portions of feed solution in an agitated glass-lined reactor. The gel was then washed twice with pure methanol, first in the agitated reactor and a second time after the gel had been removed from the reactor and placed in a six-inch column. It is important to note that, while the gel was uniformly loaded, it was not saturated with respect to hafnium. As shown in Table 1, the Hf/Zr x 100 of the feed was 2.45 while the final portion of effluent product analyzed only 1.30.

Perhaps the most significant feature of this run was the methanol washing. The two successive washings removed 1065 grams and 635 grams of oxide, respectively, from 40 pounds of gel. The Hf/Zr x 100 of the first wash was 1.4, but the second time the analysis was 2.7, which indicates that even pure methanol must have some stripping action if enough is used. Since the gel was not hafnium-saturated, it was significant that the methanol would remove material having a higher hafnium concentration than the original feed.

A second important feature of Run 6 is shown in Table 1. Jacobs' hafnium analyses of the acidified methanol strip showed that 54.7 percent of the total oxide stripped went into the acidified methanol with a lower hafnium concentration than that of the feed solution. This stripped material could thus conceivably be recycled in the adsorption cycle as feed solution, after neutralizing the acid and adding tetrachloride to give feed strength. In contrast with Run 5, where no recyclable material was obtained, this high percentage of recyclable material would seem to favor inclusion of the acidified methanol strip. However, the factor of hafnium saturation of the gel must be considered in this analysis. Runs3, 4, and 6 furnished evidence that gel unsaturated with respect to hafnium would yield low-hafnium material in the acidified methanol strip, whereas Run 5 showed that saturated gel would yield very little or nothing that could be considered recyclable. Because Run 5 most closely approximated the conditions that could be expected in normal zirconium purification operations, the indications are strong that the acidified methanol is not applicable to the gel treatment. The sulfuric acid solution could be employed as a single-step stripping to remove all the adsorbate prior to reactivation of the gel.

In such a stripping using only sulfuric acid, the zirconium on the gel that was not removed by the methanol wash would go into the acid strip along with the hafnium. The zirconium in the strip would not be directly recoverable by further purification because the acid strip obviously is not suitable for cycling through the adsorption process. Jacobs obtained the adsorbate from the acid strip by precipitating with ammonia, calcining the hydroxide to oxide, and converting the oxide back to tetrachloride by chlorination with carbon tetrachloride. Such a process could not be considered a part of gel recovery or zirconium recovery, and as much zirconium as possible would have to be recovered by methanol washing.

The amount of material removed by methanol washing should therefore be considered. In Runs 5 and 6 more material was reported washed off than would be expected from the difference between the adsorbed oxide content of gel that was methanol-washed and the content of gel not methanol-washed (Runs 3 and 4). The highest oxide content computed was 0.0825 gram oxide per gram of gel, in Run 3, against 0.065 gram oxide per gram of gel in Run 6 where two methanol washings were used. The maximum difference indicated would be approximately 300 grams of oxide (for 40 pounds of gel), considerably less than in any of methanol washings reported. This shows that some

of the material removed by methanol in Runs 5 and 6 must be attributable to poor drainage. The calculated quantity of 300 grams of oxide by methanol washing would correspond to about 20 percent of the total adsorbate-plus-occluded material on the drained gel.

In Run 6, where the gel was first methanol-washed in the glass-lined agitator, the effect of poor drainage of occluded solution was especially evident in that 1060 grams of oxide was washed off initially, followed by 675 grams when the gel was placed in a column and washed again. Of this total of 1735 grams apparently removed, only 300 grams can be accounted for definitely, and much of the other 1400 grams must have been excess occluded material owing to poor gel drainage.

In conclusion it should be stated that Jacobs' data are not applicable to calculations of zirconium loss due to the sulfuric acid stripping, because Jacobs used varying quantities of feed solution per pound of gel. This variation resulted in varying degrees of purification, so that any material balance over zirconium would be difficult to calculate. Moreover, such a zirconium loss calculation would have no direct relationship to continuous column operation where the degree of purification would be maintained constant. The computation of zirconium loss will receive attention in Analysis of Data and Results, in which zirconium loss will be related to column

operation conditions.

To summarize, the review of Jacobs' batch column data indicated the following:

1. Washing the spent gel with pure methanol, following a thorough draining of excess occluded solution, removed at least 20 percent of the total adsorbate-plus-occluded material on the gel.
2. A single agitated batch-contact washing with methanol would be preferable to a more prolonged continuous washing, and an excessive amount of methanol should be avoided. Prolonged methanol washing increased the amount of adsorbate removed from the gel, but also increased the hafnium concentration of the wash. Run 6 demonstrated that methanol has a stripping action.
3. The acidified methanol strip would not remove enough recyclable material to be economical when the methanol wash is used first. Run 5 demonstrated that, where the gel is saturated with respect to hafnium, no material is stripped which would be low enough in hafnium to merit recycling in the adsorption process as feed.

B. Proposed Treatment of Spent Gel

If the HCl-methanol strip is omitted from the treatment on economic grounds, the gel treatment would consist of methanol washing, stripping with 7N sulfuric acid, water-washing and drying, and reactivation at 300°C to desired moisture content.

The quantity of methanol that could be used in washing the spent gel, in any actual plant operation, would be fixed within rather definite limits. All the methanol used in washing may subsequently be used to make up feed solution, by adding sufficient tetrachlorides to bring the methanol wash up to feed strength. The quantities of feed solution and silica gel will be definitely related, since a certain quantity of gel will be required to purify a gallon of feed solution, fixed by the adsorption column design. From the analysis presented by Giffen (7), 2 to 4 pounds of gel might be used per gallon of solution purified, so the quantity of methanol available for washing would range from one-fourth to one-half gallon per pound of gel.

Methanol washing was studied with spent gel from the continuous adsorption column studied by Giffen. The gel was thoroughly drained of occluded feed solution by means of suction, and was placed in plastic bags kept nearly air-tight. This gel was used for the experimental work

on gel treatment in this investigation. The primary purpose of the experimental determinations on the spent gel was to determine within reasonable limits the quantities of solutions to wash and regenerate any gel. It would not be expected that ordinary variations in the gel due to its history would influence the washing and processing to any extent.

Three samples of the spent gel from the adsorption column, thoroughly drained and just sufficiently moist to be non-flowing, were washed with pure methanol as follows:

1. A single contact batchwise with methanol;
2. a multiple contact batchwise with methanol, using several portions of methanol in turn;
3. a continuous washing with methanol, using a small basket centrifuge.

Duplicate determinations of each test were made.

In Tests 1 and 2 a weighed sample of spent gel was added to a measured volume of methanol in a flask, the flask being tightly stoppered and agitated by shaking from time to time. In Test 1 a sample of the effluent solution, 5 to 10 milliliters, was withdrawn at timed intervals for determination of oxide content and hafnium analysis. Refer to Appendix 1 for a description of treatment of solution samples. At the conclusion of the washing the solution was all removed by suction on a

Buchner funnel, and the whole wash solution was treated with ammonia to precipitate the materials washed off. The precipitate was filtered, ignited to oxide and weighed.

In Test 2 the procedures were similar, except that five individual portions of solvent were used at one-hour intervals with the washings combined at the end for precipitation of the oxide.

In Test 3 the wash solution was allowed to recycle for a period of about four hours through the gel, which was in the basket of the centrifuge. The solution was then collected and treated with ammonia to precipitate the materials washed off the gel.

A notable feature of all three tests was that evaporation of the methanol took place, and was measured as the difference between the volume of washings obtained and methanol charged to the gel. For the single contact test the evaporation was about 10 percent based on the volume of methanol used. For the multiple contact test the evaporation was slightly higher, 12 to 15 percent. For the continuous test, however, evaporation amounted to about 30 per cent.

Each sample of gel, following a thorough filtering to remove the wash solution, was thoroughly stripped with a large excess (6 to 8 milliliters per gram of gel) of 7N sulfuric acid solution. The strip was removed by suction

after being allowed to contact the gel overnight, and the gel was thoroughly water-washed. The acid strip and washings were neutralized with ammonia, and the precipitate of stripped material was ignited to oxide, weighed, and analyzed for hafnium. The stripped gel was activated at 300°C to about 4% moisture and weighed as activated gel, so that the weights of washed and stripped oxides could be related to activated gel weight.

Results of the washing determinations are summarized in Table 2. In Test 1, the amount of methanol used was 0.22 to 0.25 gallon per pound of gel, and the methanol removed 24.0 to 26.6 percent of the total adsorbate-plus-occluded material from the gel. The total not washed was found from the sulfuric acid stripping. In Test 2 the methanol used was about three times that in Test 1, i.e., 0.76 gallon per pound of gel, while the methanol-washed oxide was about the same percentage of the total adsorbate-plus-occluded material. In the centrifuge washing, Test 3, poorer washing results were obtained, with only 14.0 to 14.6 percent of the total removed by methanol washing. Taking into consideration the fact that about 30 percent of the solution evaporated in Test 3, a quantity of methanol of at least 0.27 gallon per pound of gel would have been present at the end. Results comparable to those found in Tests 1 and 2 should therefore have been expected

Table 2. Washing of Spent Gel with Pure Methanol.

Test	Gal. MeOH / lb. gel	MeOH ml.	Activated wt. gel g.	MeOH washing Oxide g.	MeOH washing Hf/Zr x 100	Acid stripping Oxide g.	Acid stripping Hf/Zr x 100	% of oxides by MeOH-washing	Overall Hf/Zr x 100	Adsorbed g. oxides / g. gel
1-A	0.22	350	195	5.8	1.4	18.6	15.8	24.0	12.9	0.095
1-B	0.25	350	170	5.5	1.3	15.1	15.2	26.6	11.5	0.089
2-A	0.76	800	125	3.2	0.92	9.1	12.3	26.0	9.8	0.073
2-B	0.76	800	125	3.3	0.95	9.8	12.1	25.2	9.3	0.078
3-A	0.38	475	150	2.8	1.5	17.2	13.2	14.0	11.5	0.115
3-B	0.38	475	150	2.9	1.5	17.0	13.4	14.6	11.8	0.113

if the centrifuge method gave satisfactory washing.

It would appear that the single contact of methanol using about 0.25 gallon per pound of gel is just as efficient in washing the gel as the more elaborate washing used in Test 2, where more methanol was also used. In comparing Tests 1 and 2 there was found to be some difference in the adsorbate content of the gel and in the hafnium concentration of the adsorbate. The difference was probably due to the fact that the continuous column did not always operate at steady-state conditions, and the spent gel going out the bottom was contacting feed solution continuously so that the loading was subject to some variation. There was imperfect mixing of the gel slurry drained from the column, so that the drained and bagged gel could conceivably show gradation even within a single bag. The fact that the methanol washing removed the same proportion of total material in both cases showed the washing action of the methanol to be definite and limited in the batchwise washing used.

In Table 3 the individual timed washing results for Test 1-A are given. The results are listed in order of the cumulative time of contact between the gel and methanol wash. The values for concentration of the wash solution in grams oxide per milliliter were found from the measured samples taken from the wash at the time intervals

Table 3. Effect of Time on Batch Washing of Gel.

Test	Gal. MeOH / lb. gel	Total contact time, hours	MeOH washing g. oxides / ml. wash	Hf/Zr x 100
1-A	0.22	0.5	0.015	1.5
		1.0	0.017	1.4
		4.0	0.017	1.4
		24	0.017	1.4
		48	0.016	1.4
		72	0.016	1.3

Note: Results of 1-B were virtually identical.

indicated. The corresponding values of hafnium concentration are listed to show the slight decrease in hafnium concentration which occurred with the longer periods of batch contact between the wash solution and gel. This decrease in hafnium concentration shows that there must have been a slight adsorption of material washed off mechanically by the methanol, back onto the gel, due to the length of contact time allowed between the wash solution and gel. Even though the gel was "spent" in the nominal sense it apparently could still remove a minute amount of hafnium from the wash, which simulated a weak feed solution.

It should be noted that in Jacobs' methanol-washing of the gel a different situation prevailed, with the methanol being washed through the gel so that there was little opportunity for adsorption of washed hafnium back onto the gel. Indeed, where he used an excessive amount of methanol the tendency was for removal of more hafnium. Another factor of importance was that Jacobs was working with gel more nearly saturated with respect to hafnium than the gel being used in these small-scale tests. The small-scale tests were made to determine the importance of time, in addition to determining the amount of material removable with methanol. The hafnium concentration of the actual adsorbate would not influence either measurement to

any extent except, as noted, to show a low hafnium concentration in the wash. The most important indication from the timed samples was that the washing effect was essentially complete at 0.5 to 1 hour, there being no increase in oxides concentration after 1 hour. Time does not appear to be a very critical factor, therefore, in the methanol washing of the gel.

The determination of the quantity of 7N sulfuric acid required to strip the washed gel, and the amount of water required to wash the stripped gel, were next studied. Jacobs (10) used quantities of acid strip ranging from 0.135 to 0.5 gallon per pound of gel, with little perceptible difference in stripping efficiency. Because he used acidified methanol stripping first, however, it was necessary to establish with more certainty the quantity of sulfuric acid required when the acidified methanol strip was omitted.

Three batch contact stripping tests were made using samples of spent silica gel from the continuous adsorption column. These were washed with methanol soon after removal from the column, and removal of occluded material was complete insofar as it was possible to determine. Weighed samples of the washed gel were placed in flasks and measured volumes of 7N sulfuric acid were added. The resultant slurry was shaken by hand from time to time.

At intervals of 1, 4, and 24 hours, a 3 to 4 milliliter sample of the clear strip solution was withdrawn for determination of solute content. In all tests, there was no perceptible change noted in the concentration of stripped material in solution after 1 hour. Hence the stripping, like the batch methanol washing, does not appear to be dependent upon a time factor, provided of course that a reasonable contact between gel and strip solution be allowed.

The strip solution was removed from the gel by filtering on a Buchner funnel. The drained gel was washed with several portions of distilled water until the effluent was free of acid and a negative test for Zr-Hf was obtained with ammonia. The strip solution and washings were then neutralized with ammonia to precipitate the stripped materials, and the precipitate was ignited to oxide which was weighed and analyzed for hafnium. The gel was activated to about 4% moisture to obtain its activated weight so that the weight of stripped material could be related to activated gel weight.

Results of the stripping tests are summarized in Table 4. Comparison of the results shows that, as was noted in Table 2, there is variation in the adsorbed oxide content of the gel in the three tests. While some of this variation could be ascribed to experimental error,

such as introduction of foreign material in the precipitation or weighing error, there must also be inherent variation in gel from the adsorption column to explain the range of adsorbed oxide content in Table 4.

Table 4. Sulfuric Acid Stripping of Methanol-washed Gel.

Test	Gal. strip / Lb. gel	H_2SO_4 ml.	Activated Wt. Gel g.	Stripped oxide, g.	Adsorbed g. oxide / g. gel	Oxide Hf/Zr x 100
1-A	0.15	160	125	9.1	0.073	12.3
1-B	0.15	160	125	9.8	0.079	12.1
2-A	0.37	235	75	8.7	0.116	12.0
2-B	0.37	235	75	8.6	0.115	12.4
3-A	0.42	600	170	15.1	0.089	15.2
3-B	0.43	700	195	18.6	0.095	15.8

Variation of the amount of strip solution used, from 0.15 to 0.43 gallon per pound of gel, showed little apparent difference in stripping action. The quantity of oxides found using the largest amount of strip solution was not appreciably different from the quantity of oxide found for the smallest amount of strip. The quantity of oxides found was a maximum with the intermediate amount of strip solution, which makes the data difficult to analyze. From the deductive standpoint, the only safe conclusion

that may be drawn for stripping at this point would be that 0.15 gallon per pound of gel is too little strip solution, and 0.43 gallon per pound of gel is probably more than required. For the present it may be estimated that one-third gallon of solution per pound of gel would be a satisfactory amount to use. Subsequent treatment of gel will be made on larger batches of gel to establish more definitely the amount of strip solution required.

The final step in the processing of gel was that of washing the occluded strip solution off the gel with water. It was important to know how completely the acid could be removed with a reasonable amount of wash water using suction filtering. In the tests 1 and 3 of sulfuric acid stripping reported in Table 4, carefully measured portions of water were used (see Appendix D) and the acid washings were titrated with standardized sodium hydroxide solution (see Appendix C). The original strip solution was titrated similarly, so that the completeness of acid removal could be established by material balance. For this purpose total acidity was calculated as milliequivalents, which is the number of milliliters multiplied by solution normality determined by titration.

Results of the water-washing tests are reported in Table 5. The quantity of wash water required was observed to vary somewhat for complete washing, with more washing

Table 5. Water-washing of Stripped Gel.

Test	H_2SO_4 used ml.	N	mleq.	H_2SO_4 drain. ml.	N	mleq	Acid washings Wash ml.	Acid N	H_2SO_4 mleq.	Cumulative Gal. wash Lb. gel	Percent acid removal
1-A	160	8.50	1360	90	7.83	705	150	3.43	515	0.14	90
							170	0.77	131	0.30	99+
1-B	160	8.50	1360	110	7.70	847	150	2.70	405	0.14	92
							150	0.70	106	0.28	99+
2-A	600	7.88	4730	580	6.80	3940	350	1.59	555	0.24	94
							350	0.29	102	0.48	97
							350	0.11	39	0.72	99+
2-B	700	7.88	5520	670	6.80	4550	390	1.90	741	0.24	96
							380	0.10	38	0.46	97[a]

[a]Although removal of acid was apparently incomplete, a negative test for sulfate ion was obtained with barium chloride at the end of the test.

being required for gel stripped with a larger amount of acid strip. This was possibly due to adsorption of sulfuric acid taking place to a degree dependent upon the amount of acid present, so that more washing would be required in Test 2 where more acid was used. Water required was 0.28 to 0.30 gallon per pound of gel in Test 1, and 0.46 to 0.72 gallon per pound of gel in Test 2. Variation in the latter case was due mainly to the size of wash portions used, with three portions being required in Test 2-A (the third removing a minute amount of acid) while two wash portions were sufficient in Test 2-B.

The material balance for each determination was calculated by summing the milliequivalents of acid initially drained (suction-filtered) off the gel with milliequivalents of acid obtained by each portion of wash water used. Thus, in Test 1-A, 705 milliequivalents of acid were filtered off the gel as the strip solution and a total of 646 milliequivalents of acid were water-washed off in the two successive portions of water used. Total acid removal was therefore 1351 milliequivalents, more than 99 percent of the 1360 milliequivalents charged to the gel. In this way the percent acid removal was calculated for each washing test at the end of each wash portion used.

Because the quantity of wash water required depended, apparently, upon the amount of strip solution charged to the gel, an exact determination of washing would be more readily determined upon larger quantities of gel on which stripping performance was also determined. For the amount of acid required to regenerate the gel, it was estimated from the results in Table 5 that 0.3 to 0.4 gallon of water per pound of gel should wash the gel. Satisfactory washing would be removal of 99-plus percent of the acid, as was shown possible by the washing tests, or sufficient washing to give a negative test for sulfate ion in the wash water.

The treatment proposed for the spent silica gel, as determined by the series of small-scale tests, may be summarized as follows:

1. After thorough drainage and filtration of the gel to remove occluded solution, the gel would be washed once batchwise with pure methanol, using 0.25 gallon per pound of gel. A washing of about 1 hour, using a moderate agitation, would be satisfactory.
2. The wash solution would be removed by drainage and filtration, and the gel would then be stripped batchwise with 7N aqueous sulfuric acid,

using 0.33 gallon per pound of gel. Allowing about 1 hour, with a moderate agitation, would be satisfactory.

3. The acid strip solution would be removed by filtration, and the gel would be washed continuously with pure water until all the acid was removed from the gel. About 0.4 gallon per pound of gel would be required.

4. The final step in the gel regeneration would be removal of the excess water from the gel, activation by heating at 300°C, to obtain the gel with a moisture of about 4% by weight, wet basis. The relationship of the gel moisture to adsorptive capacity in the zirconium purification will be discussed in the next section.

C. Determination of Gel Quality

From the standpoint of controlling gel quality it was desirable to establish with some certainty how often the silica gel could be re-used, i.e., over how many cycles it could be reclaimed and still retain its adsorptive activity. Ewing and Bauer (4) demonstrated that moisture and heat of wetting could be used as criteria of water-adsorptive capacity of fresh silica gel. For a number of cycles of use, in the course of which a slight change might occur in the chemical nature of the gel, the validity of the Ewing-Bauer relationship was in some doubt. To clarify this point was the first objective of this investigation.

As a control for the gel being used in this work, and to compare results with those obtained by Ewing and Bauer, moisture and heat of wetting determinations (described in Appendix D) were made on the gel supplied by Davidson Chemical Company, Baltimore, Maryland. This gel was of a high grade of purity, with a normal moisture analysis of about 5% by weight and had a particle size range of 28 to 200 mesh.

The determination of the moisture content and heat of wetting for each gel sample are given in Table 6. Normal activation meant a temperature of 300°C (or less) to remove

a part of the adsorbed water. Addition of water to some of the samples showed that the gel could adsorb up to 32.0% moisture (wet basis) and just remain granular or free-flowing, with a heat of wetting of zero. It was interesting also that, with normal activation, the moisture content could be reduced below 3%, in some cases without any decrease in heat of wetting, by heating for a long enough period of time (3 to 4 days). The gels sintered at 600°C and at 700°C showed the effect of heating in much reduced moisture contents and heats of wetting.

Table 6. Moisture and Heat of Wetting of Fresh Silica Gel.

Normal activation 300°C		Deactivated 600°C		Deactivated 700°C	
Moisture % H_2O	ΔH_w cal. g. gel	Moisture % H_2O	ΔH_w cal. g. gel	Moisture % H_2O	ΔH_w cal. g. gel
2.5	26.4	0.8	24.0	0.23	20.4
2.6	32.9	3.2	26.1	1.2	20.2
2.9	32.8	3.9	25.7	3.1	21.8
3.2	34.2	5.0	21.4	10.7	11.2
3.7	33.4	8.3	16.5	17.6	2.6
5.9	30.2	20.0	4.2		
5.9	26.1				
6.6	23.2				
10.2	19.7				
13.3	17.6				
17.3	12.2				
22.7	5.0				
23.0	4.3				
26.9	0.5				
32.0	0.0				

Using these data a family of three curves were plotted (Figure 1) which represent the effect of gel sintering upon the heat of wetting. The data of Ewing and Bauer (4) are plotted for comparison with the normal activation curve obtained for the Davidson gel. Maximum activity of the Davidson gel was found to be somewhat higher (near 34 calories per gram) than that determined by Ewing and Bauer. The maximum also occurred at a slightly lower moisture content (about 3.5%) than they observed.

The main point of interest in Figure 1 is that the deactivation curves are similar in shape to the normal activation curve, and reflect a constant decrease of heat of wetting due to sintering. The indication is that a chemical change in the gel, or any factor which alters its adsorptive capacity other than moisture content, would alter the moisture-heat of wetting relationship from the normal. The heat of wetting may not then be a unique criterion of the condition of the gel reclaimed from the zirconium purification process.

If a change occurred in the chemical nature of the gel in the reclamation process, it would most likely be due to the adsorbed hafnium-zirconium on the gel being incompletely stripped. Other possible chemical effects might be due to the stripping reagents themselves, which probably have a negligible chemical effect on the gel

Figure 1. Activation Curves for Fresh Silica Gel.

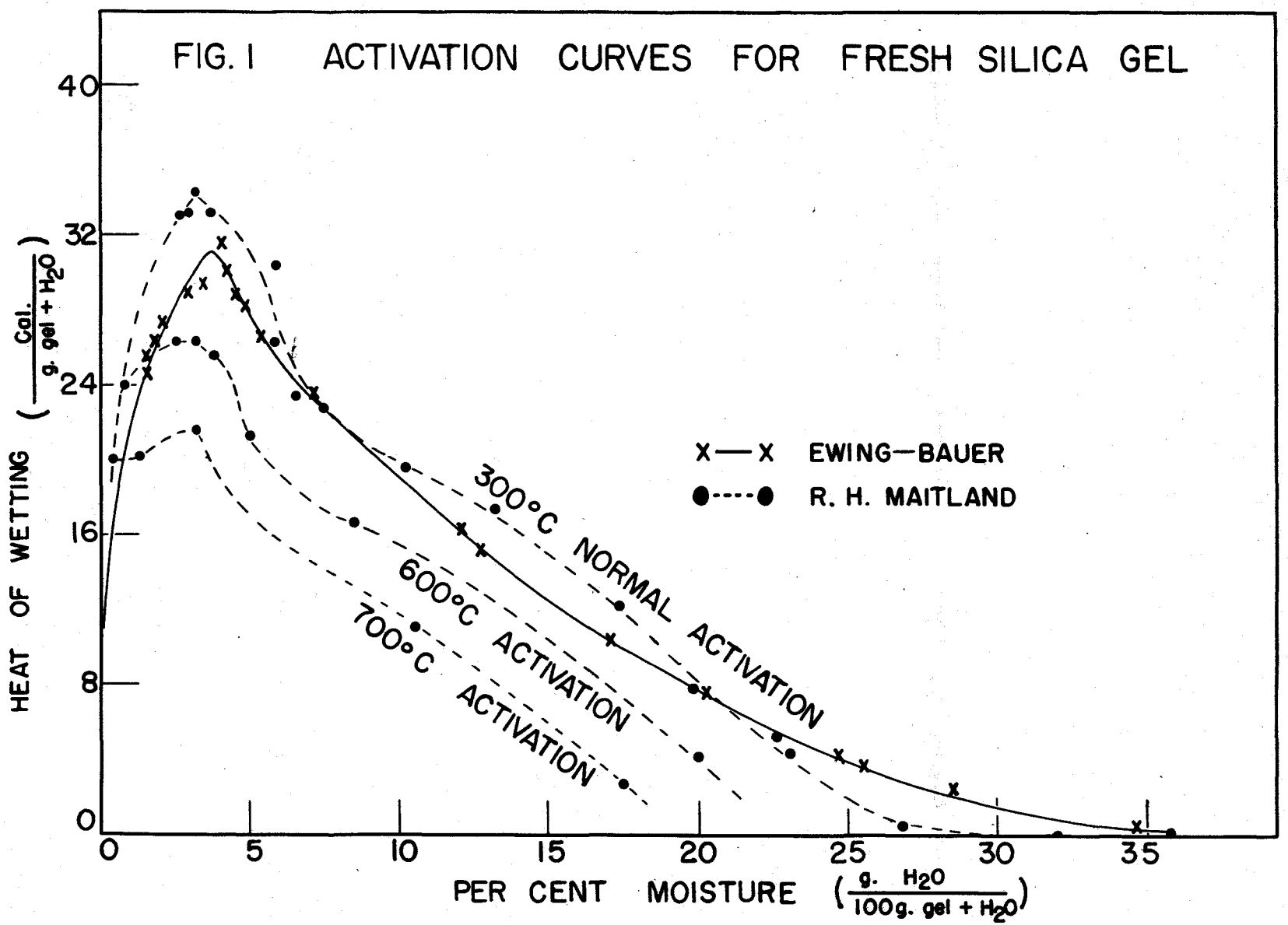
FIG. I ACTIVATION CURVES FOR FRESH SILICA GEL
HEAT OF WETTING (Cal. / g. gel + H2O)
40
32
24
16
8
0
0
5
10
15
20
25
30
35
PER CENT MOISTURE (g. H2O / 100g. gel + H2O)
X—X EWING—BAUER
●----● R. H. MAITLAND
300°C NORMAL ACTIVATION
600°C ACTIVATION
700°C ACTIVATION

itself, or to the gel reactivation which could be readily controlled to the proper temperature to prevent sintering. Interest was therefore centered upon determination of the unstripped or residual material (oxides) on the gel.

To simulate gel with unstripped adsorbate, nine samples of fresh gel were loaded with adsorbed hafnium-zirconium by contacting the gel with feed solution, and were then incompletely stripped using dilute sulfuric acid strip. The acid concentration was varied from 0.5N to 5N to obtain a different residual adsorbate on each gel sample. The incompletely stripped samples were water-washed and activated under the normal condition of 300°C to obtain a moisture content on each gel sample of near 3.5%. The heat of wetting was determined for each sample, and residual oxide was determined by hydrofluoric acid treatment. The analytical procedures used are described in Appendices D and E.

As a control on the determinations, a sample of fresh gel was run with the partially stripped samples in the hydrofluoric acid treatment. The basis of this treatment is that the silica volatilizes, leaving behind any foreign matter that may have been on the gel. The fresh gel was found to volatilize so completely that there was no preceptible residue from a 10-gram gel sample. Non-silicious mineral matter, if it was greater than the

residue indicated, apparently volatilized with hydrofluoric acid, so that there would be little error in assuming the gel to be completely volatile in residual adsorbate determinations.

To determine the effect of the residual oxide upon the activity or adsorptive capacity of the gel, a batch contact adsorption test was made on each sample of partially stripped gel according to the method described in Appendix D. A fresh gel sample was similarly tested as a control. This adsorption method allows a comparative determination of the extent of hafnium adsorption from a given quantity of feed solution in a given period of time. Adsorption was measured as a function of gel activity, using a constant quantity of feed solution and time of contact.

A standard ratio of 3 milliliters feed solution per gram of gel was used in the adsorption tests. This gave a volume of solution that could be measured out with reasonable accuracy in a graduate cylinder, for an average sample of gel (12 to 15 grams). A larger ratio of feed solution would have meant a smaller change in hafnium concentration between feed and product solution, thus minimizing the adsorption effect being measured. A smaller quantity of feed solution would have sharpened the adsorptive effect somewhat but would also have made

the gel-solution slurry more viscous, making it difficult to obtain an accurate product solution sample.

The time of contact between gel and solution was standardized at 7 days, as this was found by Baer (1) to give a contact allowing a sufficiently close approach to equilibrium conditions to be considered equilibrium for practical purposes. A 1-hour contact sample was also taken in an attempt to establish an adsorption rate comparison among the partially stripped gel samples. It was thought that adsorption rate would decrease with increased residual oxide, and that the rate decrease would be shown by smaller change from the degree of hafnium adsorption at 1 hour to that at 7 days.

At the end of the 7-day contact period the gel and product solution were separated from one another by filtration on a Buchner funnel. The volume of product solution was measured, and was always found to be smaller than the volume of feed charged initially to the gel. The reduction in volume was undoubtedly due to the adsorptive effect, and was greater with the more completely stripped gel samples.

The filtered spent gel was treated according to the method described in Appendix D. The methanol wash and sulfuric acid strip solutions obtained were treated with ammonia to obtain the oxides content. The sulfuric acid

strip used in this case was the normal concentration (7N) recommended for complete stripping of gel.

After reactivation of the gel samples to approximately 3.5% moisture, a repeat hydrofluoric acid treatment was made on each sample. This determination was made for two principal reasons:

1. To check the residual oxide after stripping and establish whether or not stripping with 7N sulfuric acid reduces residual oxide from a previous incomplete stripping.
2. To establish a material balance over the adsorption cycle, and thereby ascertain the accuracy or validity of the data.

Table 7 is a summary of the data obtained for the nine gel samples having a residual oxide, and the control sample of fresh gel. The residual oxide varied from 0 (fresh gel) to 0.0675 gram of oxide per gram of gel plus oxide, with the ten runs listed in the table in order of increasing residual oxide. The heats of wetting are seen to be quite erratic with respect to the amount of residual oxide on the gel, and demonstrate the fact that heat of wetting would not be a reliable criterion of gel quality. The variability may be due in part to slight difference in moisture content, and in particular to the unknown relationship between the residual oxide and moisture.

If the residual oxide itself had a heat of wetting, this would explain the high heats of wetting with some of the partially stripped gels. Whatever the cause, the lack of correlation between heat of wetting and residual oxide shows that heat of wetting would not be a reliable criterion of gel quality.

The properties of the product solution obtained from the batch contact adsorption test are given as the factors x_p, R_p and v_p. The term x_p is the total oxide concentration in grams per ml. of the product solution, whose volume is v_p in milliliters per gram of gel charged. R_p is the hafnium concentration in the product oxide, in weight percent. Corresponding terms for the feed solution are x_F, R_F and v_F. Properties of the feed solution used are given in notes at the bottom of Table 7.

It should be noted that the term R will be used in subsequent tables to refer to hafnium concentration as the Hf/Zr x 100 ratio as reported for oxides by the Spectrographic Laboratory. Where the value of the Hf/Zr x 100 ratio is small, i.e., 5 or less, the numerical value is practically equivalent to percentage of hafnium. Thus, if the Hf/Zr x 100 is 1.0, this oxide is 0.99% hafnium; if the Hf/Zr x 100 is 5.0, the oxide is 4.76% hafnium. With values over 5 there is increasing divergence between the numerical values of Hf/Zr x 100 and equivalent percentage

Table 7. Adsorption Testing of Silica Gel with Known Residual Oxide.

Resid. ox. g. oxide / g. ox. gel	H_w cal. / g.gel	Product solution at 7 days: xp g. ox. / ml.	R_p	vp ml. / g.gel	S_H v_F / v_p	S_H $x_F R_F v_F / x_p R_p v_p$	Material Balance: xpvp g.oxide / g. gel	MeOH wash g. oxide / g. gel	Strpd. gel Acid strp. g.oxide / g. gel	Strpd. gel loading g.oxide / g. gel	Material balance error, %
0	30.9	0.119	0.8	1.80	1.67	5.63	0.214	0.087	0.125	0.002	-2.28
0.0116	27.0	0.122	1.1	1.92	1.56	3.73	0.234	0.086	0.153	0.0116	+ 7.80
0.0123	26.3	0.123	1.0	2.01	1.49	3.89	0.247	0.084	0.118	0.0120	+ 2.37
0.0125	34.2	0.119	1.1	2.02	1.48	3.65	0.240	0.089	0.157	0.0120	+ 10.5
0.0159	26.7	0.126	1.0	2.05	1.46	3.74	0.258	0.088	0.147	0.0144	+ 11.8
0.0220	25.2	0.126	1.1	2.06	1.45	3.36	0.260	0.086	0.119	0.0016	+ 1.41
0.0310	35.0	0.122	1.3	2.10	1.43	2.90	0.256	0.082	0.119	0.0063	- 1.22
0.0355	32.5	0.122	1.3	2.14	1.40	2.85	0.261	0.081	0.118	0.0075	- 1.27
0.0504	33.5	0.127	1.4	2.20	1.36	2.46	0.280	0.084	0.125	0.0092	+ 2.04
0.0675	31.7	0.127	1.5	2.20	1.36	2.31	0.280	0.090	0.140	0.0121	+ 3.09

Notes: Feed Solution: x_F = 0.146 g. oxide/ml.
R_F = 2.2 Hf/Zr x 100
v_F = 3.0 ml./g. gel

of hafnium. Where low-hafnium oxides are involved, as with product and feed solutions, the Hf/Zr x 100 can be used as percent of hafnium. In Appendix B equations will be found for converting Hf/Zr x 100 to percent hafnium where this is required, for values over 5.

The extent to which the residual oxide influenced hafnium concentration and total oxides concentration is evident from an inspection of Table 7. The total oxides xp changed comparatively little, about 15 percent, while Rp changed 100 percent. The effect of increased residual oxide was thus a small decrease in the total adsorptive capacity of the gel, and a large decrease in the hafnium adsorptive capacity. It may therefore be stated that the gel loses its capacity to purify much sooner than it loses its total adsorptive capacity.

The reduction in the hafnium content from the feed to the product solution is proportional to the purifying capacity or activity of gel. In batch contact adsorption a standardization in the time of contact and in the quantity of solution used per gram of gel was required, in order to make the gel condition the only variable. A ratio called the hafnium adsorption factor

$$S_H = \frac{x_F R_F v_F}{x_p R_p v_p}$$

may then be used as a comparative factor by which the hafnium content of the feed is reduced by the gel. The hafnium adsorption factor is the ratio of the grams of hafnium in the feed per gram of gel divided by the grams of hafnium in the product per gram of gel. In Table 7 the hafnium adsorption factor is seen to decrease with increased residual oxide content of the gel, as would be expected. With the fresh gel (control) the hafnium in solution was reduced by a factor of 5.63 during the standard 7-day contact period, while with the gel having the highest residual oxide the reduction factor was only 2.31.

In addition to the data taken for the standard 7-day contact, adsorption data were also taken for contact at 1 hour. It was found, however, that the values of x_p and R_p showed so little change from the feed conditions that these data were of little value in calculating an accurate value for adsorption factor at 1 hour. Moreover, the volume of solution at 1 hour could not have been determined without interrupting the adsorption contact to determine v_p. Data for the 1-hour contact are therefore not reported in Table 7.

In Figure 2 the hafnium adsorption factor is graphed as a function of residual oxide on the gel. It is apparent that relatively small amounts of unstripped adsorbate will reduce the adsorption factor considerably, and this

Figure 2. Adsorption Characteristics of Incompletely Stripped Silica Gel.

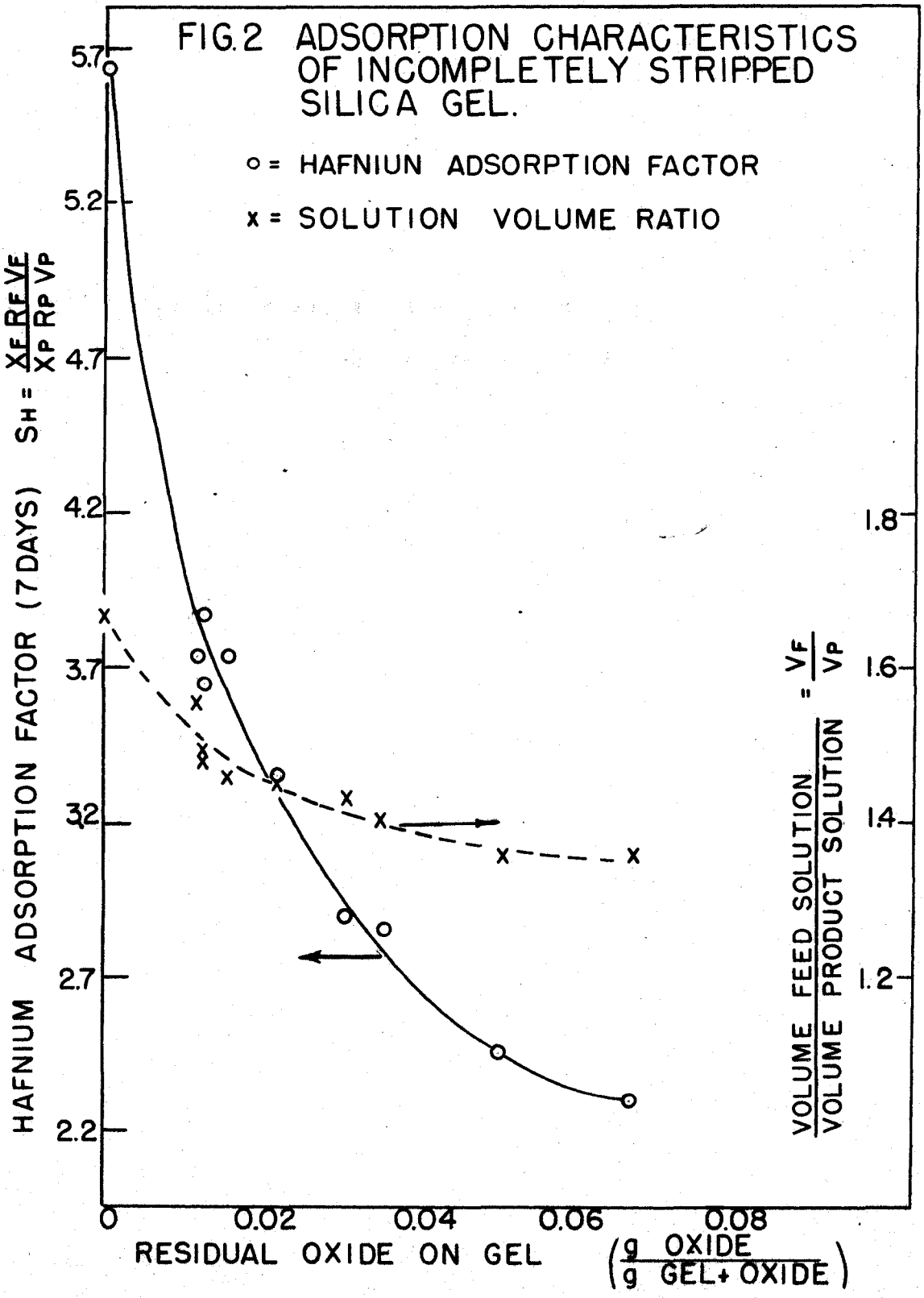
FIG. 2 ADSORPTION CHARACTERISTICS OF INCOMPLETELY STRIPPED SILICA GEL.
o = HAFNIUN ADSORPTION FACTOR
x = SOLUTION VOLUME RATIO
HAFNIUM ADSORPTION FACTOR (7 DAYS) $S_H = \frac{X_F R_F V_F}{X_P R_P V_P}$
5.7
5.2
4.7
4.2
3.7
3.2
2.7
2.2
1.8
1.6
1.4
1.2
$\frac{\text{VOLUME FEED SOLUTION}}{\text{VOLUME PRODUCT SOLUTION}} = \frac{V_F}{V_P}$
0
0.02
0.04
0.06
0.08
RESIDUAL OXIDE ON GEL $\left(\frac{g\ \text{OXIDE}}{g\ \text{GEL+OXIDE}}\right)$

probably means that the most active purifying surface of the gel is strongly influenced by the residual material, probably by being blocked off mechanically. The importance of good gel stripping, to maintain the purifying capacity as high as possible, is emphasized by this curve.

On the same graph the solution volume ratio v_F/v_P is also plotted against residual oxide content. The volume of solution was observed to decrease during the adsorption, with a large decrease in the case of low-residual oxide gels, and comparatively small decrease with the gels having high residual oxide. It was therefore considered that the ratio of volumes might be as good a measure as S_H for the purifying capacity of the gel, and would be simpler to determine. The correlation of v_F/v_P with residual oxide was found to be much less sensitive, however, than the correlation of S_H with residual oxide. The range of volume ratios was only 1.67 to 1.36, while the corresponding range of adsorption factor was 5.63 to 2.31. The adsorption factor thus appears to be a better index to purifying capacity of the gel than does the solution volume ratio.

The final five columns in Table 7 give the data on oxide found in the product, methanol wash, and sulfuric acid strip, and the residual oxide found on the stripped gel. These data enabled a material balance to be

established over each of the adsorption runs. The material balance was made on the basis of the weight of oxide per gram of partially stripped gel charged to the adsorption, as follows:

Oxide in feed	+	Oxide on gel	=	Oxide in product	+	Oxide in methanol	+	Oxide in sulfuric acid	+	Oxide on stripped gel

The difference between total oxide obtained and total oxide fed was divided by the total oxide fed to obtain the percent difference or error in the material balance. Table 7 shows that most of the errors came out positive, showing an apparent gain in oxide for the system. It may be noted that, where most of the errors were large and positive, there was a correspondingly large figure for the oxide weight found in the sulfuric acid strip. Error in the stripping procedure, possible introduction of foreign matter in the precipitation of the oxide, or even an error in weighing the oxide, might be responsible for variation in the figures.

For the ten adsorption runs the material balance error was found to range from 1.22 percent to 11.8 percent with an arithmetic average of 4.60 percent error. So far as the relative accuracy of the adsorption data is concerned, the runs having larger material balance errors did not show any great divergence from the curves plotted in

Figure 2. The results obtained would thus seem to be reliable.

The check determinations of residual oxide on the stripped gel were interesting in that they showed residual oxide in most cases was reduced after the stripping. It must therefore be concluded that in cases of incompletely stripped gel, i.e., gel that has been activated with residual adsorbate, a considerable part of the residual oxide can be reduced by the next stripping cycle. This would be of some value in gel recovery, though it would be poor economy to rely on reclaiming gel in a subsequent stripping after it had been inadequately stripped and used in an intervening adsorption cycle. The poor performance in the intervening adsorption would more than cancel any saving of acid in the inadequate stripping.

It should be pointed out that the values of stripped gel residual oxide listed in Table 7 are based on the starting weight of gel charged to the adsorption runs. Because of the fact that the gel weight changed slightly, due to the removal of some of the residual oxide in the stripping, conversion to starting gel weight was necessary in order that the oxide weights could be added directly to give the "output" for material balance calculation. The weight of oxide removed by the sulfuric acid strip also included, it should be noted, the weight of

residual oxide removed along with the adsorbate. For the material balance it was more convenient to list stripped oxide as a total than to attempt to resolve it into true adsorbate and residual material. In either event the material balance error would have been the same, since the material balance was calculated on total oxide obtained. If an error was introduced in determination of stripped oxides, as was considered possible for some of the large errors, it would not have been possible to detect it by any calculation (except, of course, by material balance itself).

Probably the most important conclusion from this group of adsorption runs is that residual oxide due to insufficient stripping of the gel reduces the purifying capacity of the gel but not necessarily the total adsorptive capacity. This may be considered as a change in the chemical nature of the gel, the result being that a property such as heat of wetting is not a sensitive criteria of the purifying capacity. A relatively small amount of residual material produces a comparatively large change in the purifying capacity of the gel.

A study was next made on the effect of the sulfuric acid strip treatment to determine if the gel undergoes any discernable chemical change due to this treatment alone. A fresh sample of silica gel was activated at

300°C, and the moisture and heat of wetting were determined merely as a check on activation. The gel was then treated with sulfuric acid strip solution as it would be if it were spent gel (Appendix D). The treatment was repeated over several cycles and from each cycle, after the water-washing and reactivation, a ten-gram sample of gel was set aside for a 7-day batch contact adsorption test. The adsorption tests were then made under controlled conditions as before, to determine if the acid treatments produced any progressive change in the purifying capacity of the gel.

The results of these adsorption determinations are summarized in Table 8. Two series of experiments are reported, and are designated as A and B respectively. Each was begun with fresh gel. In the A series the gel was completely water-washed after each acid contact, while in the B series the gel was purposely washed incompletely to determine the effect, if any, of the residual acid. To save time the adsorption tests were first made on gel from alternating cycles of contact for each series. It was found that the values of 7-day hafnium adsorption factor S_H calculated for each adsorption varied little from the fresh gel to the end of each series of tests. Values of S_H ranged from 3.84 to 3.61, and there was no consistent variation noted in either series of tests.

These results were obtained on gel from the odd-numbered cycles, and since there was no change of importance it was not considered worthwhile to test the gel from the other cycles.

Table 8. Effect of the Sulfuric Acid Strip Solution on the Purification Capacity of Silica Gel.

Cycle	% H_2O*	ΔH cal./g.gel	7-day Product x_p	R_p	v_p	$S_H = \frac{x_F R_F v_F}{x_p R_p v_p}$
A-1	3.23	31.6	0.122	1.05	1.87	3.84
A-3	2.83	32.6	0.121	1.1	1.86	3.70
A-5	3.90	31.9	0.123	1.1	1.85	3.68
A-7	3.69	31.4	0.122	1.1	1.84	3.72
B-1	3.69	31.4	0.127	1.1	1.83	3.61
B-3	3.13	30.2	0.118	1.1	1.84	3.84
B-5	3.57	30.1	0.123	1.1	1.85	3.68

Notes: Feed Solution: x_F = 0.146 g. oxide/ml.
R_F = 2.2 Hf/Zr x 100
v_F = 3.0 ml./g. gel

*Moisture and heat of wetting values are averages of 3 determinations on each sample.

The conclusion from the adsorption results was that the gel underwent no perceptible consistent change as a result of the sulfuric acid strip itself. It would therefore appear that the stripping can be dismissed as a possible cause of reclaimed gel having a lower purifying capacity than fresh gel. Compared to the effect of residual

oxide, the effect of the sulfuric acid would be insignificant. Even in the B series of tests, in which residual acid was purposely left on the gel, there was no discernable effect noted due to this acid.

Having thus far established that the condition of the gel is dependent mainly upon unstripped material remaining before reactivating the gel, interest was centered upon evaluation of the actual stripping of spent gel over a number of cycles of gel use. Evaluation of stripping could be made by either a determination of residual oxide or an adsorption test of the reclaimed gel under controlled conditions.

Before studying the stripping operation on a pilot plant scale, several preliminary small-scale studies were made on gel that was successively adsorption-tested and stripped over several cycles. The experimentation was begun with five samples of fresh gel activated normally. Moisture and heat of wetting were determined for each gel sample merely as a check on the activation. The 7-day batch contact adsorption test was then made on each sample of gel, as described in Appendix D. The spent gel samples were then methanol-washed, stripped with sulfuric acid using 3 milliliters strip per gram of gel, water-washed and reactivated for the next adsorption cycle. The details of the stripping are given in Appendix 4e. Five

cycles of adsorption loading and stripping were obtained, including the initial one, for each gel sample.

Results of the five adsorption cycles are summarized in Tables 9 through 13, respectively. In each table the gel samples are listed in the order of increasing moisture content, as a matter of format. Three replicate determinations were made on each sample of gel for moisture, heat of wetting and adsorption. The adsorption results are listed separately, and the moisture and heat of wetting are each arithmetic averages of the three determinations on each sample.

From the adsorption data the value of the hafnium adsorption factor S_H was calculated for each run. From an examination of S_H values over the five adsorption cycles, two conclusions are immediately apparent. First, of course, there was a general decline in the value of the adsorption factor, and therefore in the purifying capacity of the gel, the more the gel was used. Secondly, the reproducibility of S_H was not too good among the three determinations performed on each sample of gel. The range in S_H values was about ten percent for each sample tested, with better reproducibility than this in a few cases. Of the total of 25 sample tests (75 replicate determinations), tests showed a range in adsorption factor values of ten percent or more, and the other 10 tests showed a better check than this.

Table 9. Adsorption Tests on Silica Gel, Cycle 1.

% H_2O	ΔH_w cal./g.gel	Product Solution at 7 days x_P g.ox./ml.	R_P	v_P ml./g.gel	$x_P v_P$ g.ox./g. gel.	Methanol wash g. oxides/g. gel.	H_2SO_4 strip g. oxides/g. gel	S_H	$\frac{x_P R_P v_F}{x_P R_P v_P}$	Material Balance Error, %
		0.112	0.80	1.84	0.206	0.084	0.107		5.20	-2.70
2.64	33.5	0.112	0.74	1.84	0.206	0.085	0.125		5.42	+1.96
		0.110	0.72	1.89	0.208	0.080	0.130		5.74	+2.45
		0.110	0.71	1.74	0.191	0.086	0.129		6.29	-0.49
4.08	35.6	0.108	0.69	1.80	0.194	0.088	0.132		6.36	+1.42
		0.107	0.68	1.75	0.187	0.089	0.134		6.74	+0.49
		0.109	0.71	1.80	0.196	0.083	0.142		6.15	+3.18
6.19	32.1	0.107	0.63	1.87	0.200	0.082	0.143		6.77	+4.16
		0.105	0.71	1.93	0.203	0.082	0.128		5.95	+1.22
		0.107	0.88	1.87	0.200	0.084	0.144		4.86	+4.90
7.36	29.5	0.107	0.86	1.90	0.203	0.080	0.119		4.89	-1.37
		0.106	0.89	1.92	0.204	0.070	0.167		4.72	+8.08
		0.106	0.93	1.99	0.211	0.074	0.142		4.30	4.63
8.0	26.8	0.106	0.91	1.95	0.207	0.073	0.117		4.55	2.69
		0.104	0.94	2.00	0.208	0.068	0.164		4.38	7.82

Notes: Feed solution: x_F = 0.136 g. oxide/ml.
R_F = 2.1 Hf/Zr x 100
v_F = 3.0 ml/g. gel

Table 10. Adsorption Tests on Silica Gel, Cycle 2.

% H_2O	ΔH_w cal./g.gel	Product solution at 7 days x_p g.ox./ml.	R_p	v_p ml./g. gel.	Prod. oxide $x_p v_p$ g.ox./g.gel	Methanol wash g. oxides/g. gel	H_2SO_4 strip g. oxides/g. gel	S_H	$\frac{x_F R_F v_F}{x_p R_p v_p}$	Material Balance Error, %
		0.115	1.0	2.00	0.230	0.050	0.150		3.72	+5.40
4.93	33.3	0.114	0.88	2.05	0.234	0.040	0.162		4.15	+6.85
		0.113	0.88	2.00	0.226	0.056	0.150		4.30	+5.88
		0.117	0.77	1.92	0.225	0.042	0.156		4.95	+3.67
5.52	34.6	0.116	0.88	1.95	0.226	0.040	0.158		4.30	+3.91
		0.115	0.69	1.90	0.218	0.030	0.181		5.68	+5.00
		0.116	0.85	1.78	0.206	0.060	0.170		4.88	+4.40
5.67	32.2	0.112	0.77	1.91	0.214	0.060	0.154		5.20	+2.44
		0.105	0.89	1.90	0.199	0.066	0.156		4.81	+0.73
		0.112	0.85	2.01	0.225	0.055	0.159		4.45	+7.59
7.02	28.0	0.109	0.97	2.05	0.223	0.050	0.167		3.96	+7.82
		0.108	0.75	2.10	0.227	0.064	0.136		5.04	+4.65
		0.115	1.1	2.25	0.259	0.031	0.142		3.00	+5.88
8.6	24.4	0.113	0.79	2.22	0.251	0.040	0.131		4.35	+3.43
		0.110	0.96	2.20	0.242	0.045	0.127		3.68	+1.47

Notes: Feed Solution: x_F = 0.136 g. oxide/ml.
R_F = 2.1 Hf/Zr x 100
v_F = 3.0 ml./g. gel

Table 11. Adsorption Tests on Silica Gel, Cycle 3.

% H_2O	ΔH_w cal./g.gel.	Product solution at 7 days x_p g.ox./ml.	R_p	v_p ml./g.gel	Prod. Oxide $x_p v_p$ g.ox./g.gel	Methanol wash g. oxides/g. gel	H_2SO_4 strip g. oxides/g. gel	S_H $\frac{x_F R_F v_F}{x_p R_p v_p}$	Material Balance Error, %
		0.124	0.96	2.05	0.254	0.057	0.112	3.51	+3.67
3.06	21.5	0.123	0.89	2.12	0.261	0.055	0.111	3.70	+4.65
		0.122	0.89	2.12	0.258	0.060	0.106	3.72	+3.90
		0.126	1.0	2.20	0.277	0.042	0.105	3.08	+3.92
3.06	20.4	0.124	1.1	2.23	0.276	0.041	0.109	2.82	+4.40
		0.122	1.0	2.20	0.268	0.055	0.105	3.20	+4.90
		0.124	1.2	2.23	0.277	0.054	0.092	2.90	+3.67
3.57	20.2	0.121	1.1	2.20	0.266	0.054	0.101	2.94	+3.18
		0.120	1.1	2.23	0.267	0.052	0.105	2.92	+3.92
		0.122	1.1	2.30	0.280	0.040	0.105	2.78	+4.65
4.43	21.2	0.122	1.1	2.22	0.270	0.041	0.117	2.88	+4.90
		0.122	1.0	2.20	0.268	0.035	0.132	3.18	+6.61
		0.116	1.0	2.14	0.248	0.030	0.158	3.44	+6.85
4.67	33.2	0.116	1.0	2.08	0.241	0.030	0.165	3.54	+6.85
		0.116		2.08	0.241	0.031	0.163	3.85	+6.61

Notes: Feed solution: x_F = 0.136 g. oxide/ml.
R_F = 2.1 Hf/Zr x100
v_F = 3.0 ml./g. gel

Table 12. Adsorption Tests on Silica Gel, Cycle 4.

% H_2O	ΔH_w cal./g.gel.	Product solution at 7 days x_P g.ox./ml.	R_P	v_P ml./g.gel	Prod. oxide $x_P v_P$ g.ox./g.gel	Methanol wash g. oxides/g. gel	H_2SO_4 Strip g. oxides/g.gel	$SH\frac{x_F R_F v_F}{x_P R_P v_P}$	Material Balance Error, %
		0.161	1.0	2.28	0.367	0.047	0.099	2.32	+2.40
2.53	18.9	0.159	1.1	2.30	0.366	0.052	0.082	2.02	-0.20
		0.155	1.0	2.31	0.358	0.051	0.094	2.38	+0.40
		0.160	1.0	2.30	0.368	0.050	0.075	2.31	-1.60
3.26	16.0	0.159	1.0	2.31	0.367	0.049	0.087	2.31	+0.40
		0.157	1.0	2.35	0.369	0.050	0.078	2.31	-0.80
		0.162	1.1	2.35	0.381	0.050	0.091	2.03	+4.19
3.48	17.5	0.161	1.1	2.32	0.373	0.052	0.071	2.05	-1.00
		0.150	1.0	2.34	0.351	0.050	0.090	2.28	+1.99
		0.164	1.0	2.30	0.377	0.050	0.089	2.25	-3.00
3.86	15.1	0.157	1.1	2.31	0.363	0.051	0.071	2.13	-3.15
		0.156	1.0	2.30	0.359	0.049	0.081	2.38	-2.39
		0.155	0.97	2.26	0.350	0.055	0.110	2.52	+2.79
4.60	22.9	0.154	0.94	2.26	0.348	0.052	0.106	2.60	+1.00
		0.152	0.87	2.22	0.337	0.054	0.110	2.90	0

Notes: Feed Solution: x_F = 0.167 g. oxide/ml.
R_F = 1.7 Hf/Zr x 100
v_F = 3.0 ml./g. gel

Table 13. Adsorption Tests on Silica Gel, Cycle 5.

% H_2O	ΔH_w cal./g.gel	Product solution at 7 days x_P g.ox./ml.	R_P	v_P ml./g.gel	Prod. oxide $x_P v_P$ g.ox./g.gel	Methanol wash g. oxides/g. gel	H_2SO_4 Strip g. oxides/g.gel	$S_H = \frac{x_F R_F v_F}{x_P R_P v_P}$	Material Balance Error, %
		0.162	1.1	2.25	0.364	0.050	0.075	2.12	-2.40
2.51	16.6	0.161	1.2	2.25	0.362	0.050	0.076	1.97	-2.59
		0.158	1.0	2.29	0.362	0.052	0.070	2.36	-3.39
		0.161	1.2	2.32	0.373	0.050	0.080	1.92	+0.40
2.56	16.1	0.159	1.0	2.38	0.378	0.049	0.083	2.24	+1.80
		0.151	1.1	2.32	0.350	0.060	0.071	2.22	-4.00
		0.160	1.1	2.30	0.368	0.055	0.069	2.10	-1.80
2.82	16.5	0.158	1.1	2.34	0.370	0.055	0.086	2.09	+2.00
		0.158	1.1	2.31	0.365	0.058	0.081	2.12	+0.60
		0.158	1.1	2.28	0.360	0.061	0.081	2.14	+0.40
3.10	19.1	0.155	1.2	2.29	0.355	0.060	0.086	2.16	0
		0.151	1.1	2.30	0.347	0.061	0.077	2.23	-3.19
		0.160	1.0	2.30	0.368	0.049	0.093	2.31	+1.80
3.11	18.9	0.157	1.0	2.33	0.366	0.050	0.091	2.33	+1.20
		0.156	0.98	2.31	0.358	0.050	0.094	2.40	+0.40

Notes: Feed Solution: x_F = 0.167 g. oxide/ml.
R_F = 1.7 Hf/Zr x 100
v_F = 3.0 ml./g. gel

The reason for this variability in S_H can be established with little difficulty from the adsorption data, these being the factors x_p, R_p and v_p, which were used to calculate S_H. The determinations of x_p, the oxide concentration of the product solution, as well as the product solution volume v_p, showed very good reproducibility. The values of R_p, the Hf/Zr x 100 ratio established by spectrographic analysis of the product oxide, was found to be the factor causing most of the variation in results. While spectrographic analyses were supposedly accurate to within five percent, greater variation than this was found in some cases.

A hafnium balance over the adsorption was considered as a means of checking the validity of the adsorption results. A hafnium balance could be obtained as:

Hafnium in feed	=	Hafnium in product	+	Hafnium in methanol	+	Hafnium in sulfuric acid

in which each item would be obtained by multiplying the weight of oxide found by the respective hafnium analysis in percent. Such a method would have the disadvantage of requiring reliable spectrographic analyses for hafnium in the methanol-wash and acid strip oxides, to check a possible error in the spectrographic analysis for hafnium in the product. Because the analyses were all subject to

the same potential error, it would be meaningless to attempt to isolate one such error by calculations involving other errors possibly as large.

As a means of obtaining some check on the adsorption data validity, an overall oxide balance was made on each adsorption run. In Tables 9 through 13 the data on oxide obtained from product solution, methanol wash and sulfuric acid strip are tabulated in three consecutive columns. The basis used throughout was grams of oxide per gram of gel charged to the adsorption (gel plus any residual oxide it might have) to obtain:

$$\text{Oxide in feed} = \text{Oxide in product} + \text{Oxide in methanol} + \text{Oxide in sulfuric acid}$$

Subtracting the oxide feed from the total oxide obtained, and dividing the difference by the oxide fed, gave the material balance error in percent.

The material balance error is given for each adsorption run in Tables 9 through 13. A positive error was again found for many of the oxide balances, indicating an apparently greater total oxide output than oxide fed. As in the cases noted in Table 7, most of the larger positive errors occur where the weight of oxide found in the sulfuric acid strip was unduly large, i.e., larger than most of the other values of oxide weight in that column.

The indication, therefore, is that in the stripping, or in the precipitation or weighing of the stripped material a positive error is introduced in a few cases which shows up as a positive material balance error.

Negative values of error indicated a deficiency of oxide obtained in the material balance, which would be expected if some of the oxide was left behind on the gel by the sulfuric acid strip. Residual oxide will be discussed below. The main conclusion to be drawn from the material balance errors is that, because the error was generally in the range of five percent or less, the variability in the hafnium adsorption factor S_H was due mainly to the corresponding variability in the product hafnium analysis. There was no correlation between material balance error and variability of S_H that would have enabled unlikely values of S_H to be rejected on the basis of the oxide balance error.

The most important relationship to be established by the series of adsorption tests on silica gel over several cycles, it would appear, was that the hafnium adsorption factor decreased with use of the gel. In Figure 3 all values of S_H obtained in each cycle of gel testing are plotted against the respective cycle number. An arithmetic average value was calculated and plotted for each cycle, and a straight-line curve drawn through the average points

Figure 3. Hafnium Adsorption Factor Over Five Adsorption Cycles. Gel Stripped Once After Each Cycle.

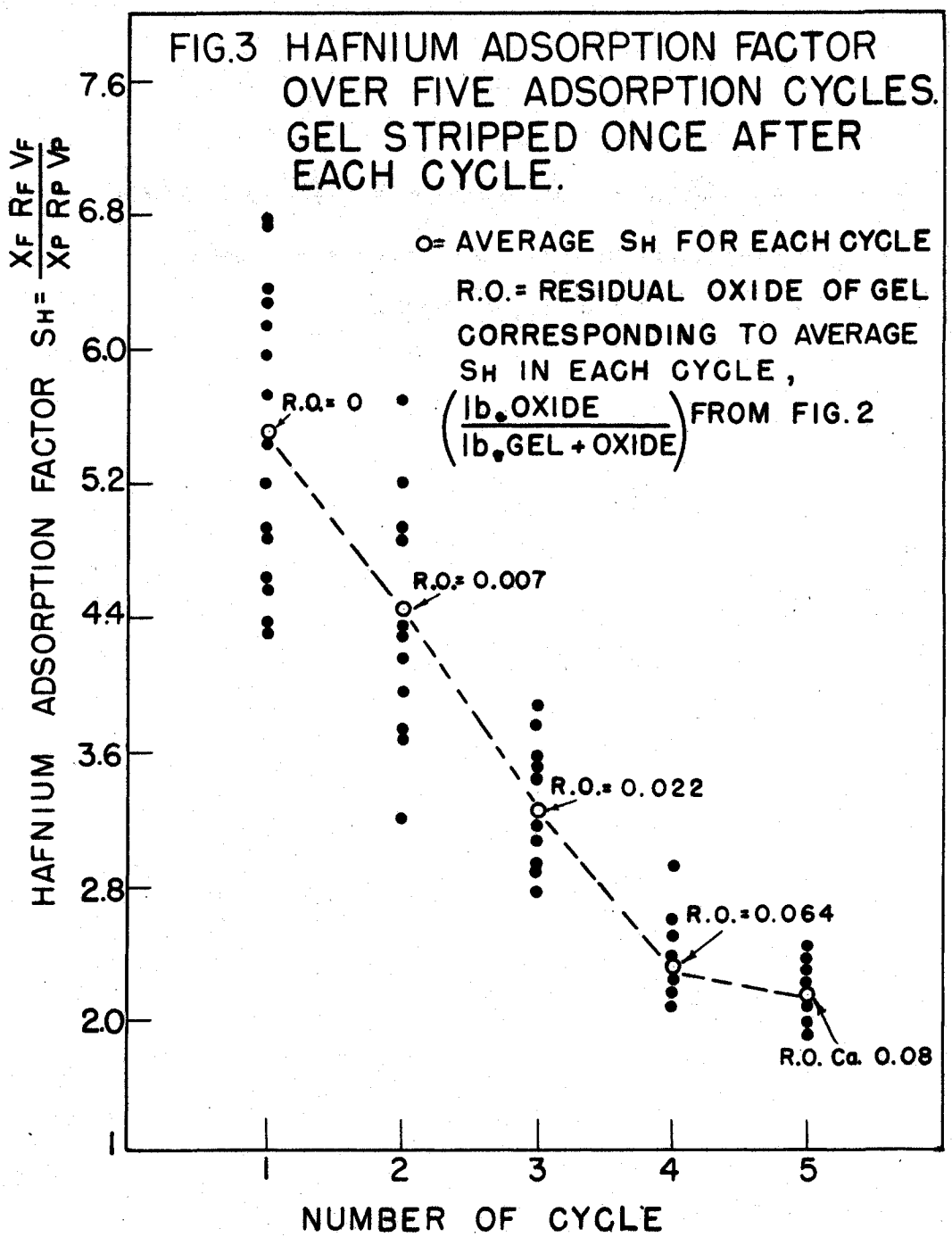
FIG.3 HAFNIUM ADSORPTION FACTOR OVER FIVE ADSORPTION CYCLES. GEL STRIPPED ONCE AFTER EACH CYCLE.
O= AVERAGE SH FOR EACH CYCLE
R.O.= RESIDUAL OXIDE OF GEL CORRESPONDING TO AVERAGE SH IN EACH CYCLE, (lb. OXIDE / lb. GEL + OXIDE) FROM FIG. 2
R.O.= 0
R.O.= 0.007
R.O.= 0.022
R.O.= 0.064
R.O. Ca. 0.08
HAFNIUM ADSORPTION FACTOR SH = XF RF VF / XP RP VP
7.6
6.8
6.0
5.2
4.4
3.6
2.8
2.0
1
1
2
3
4
5
NUMBER OF CYCLE

to show the trend of decrease. The graph shows that the decrease in average adsorption factor was about linear between the first four cycles, and that the average adsorption factor decreased to less than one-half its initial value over the five cycles of testing.

If Figure 3 is compared with Figure 2, the correlation of adsorption factor with residual oxide, values of residual oxide content may be spotted on Figure 3 for the values of average S_H in each cycle. These values of residual oxide are indicated on Figure 3, and they show that the residual oxide increased from 0.007 gram per gram of gel after the initial cycle to 0.08 gram per gram of gel after the fifth cycle. There was a three-fold increase in residual oxide in each of the two cycles following the second cycle, except that from cycle 4 to 5 the increase was quite small. Incompleteness of gel stripping is indicated from the consistent increase in residual oxide. Individual determinations of the residual oxide were not made on each sample after each cycle, as this would have been extremely time-consuming, and would have required tremendous gel samples to allow five cycles to be obtained with a residual oxide determination after each.

It is a rather major contradiction that the oxide material balances found in many of the adsorption runs were positive, whereas the decrease in volume of hafnium

adsorption factor indicated (Figure 3) that residual oxide was present on the gel in each cycle after the initial cycle. It would have been expected that residual oxide would have been shown by negative material balance errors, i.e., a deficiency in the "output" oxide. No doubt the reason for the material balance failing to accurately indicate the completeness of the stripping was that the quantity of residual oxide was generally small in comparison with the total inventory entering the balance. In particular, the amount of oxide removed by the acid strip was quite large and any appreciable variation could well mask a deficiency due to residual oxide. Such variations in stripped oxide weight already have been noted in Tables 7 and 9 through 13, and it was pointed out that undue variations in the weight of stripped oxides caused large positive errors in the oxide material balance.

Because the stripping appeared to be at fault in a number of the runs in this series of tests, it was decided to repeat the series of small-scale batch adsorption tests using a slightly modified stripping procedure. In the previous series the gel was stripped with a single portion of 3 milliliters of sulfuric acid solution per gram of gel charged to the adsorption. It was considered that dividing the strip solution into two parts and using them in succession would give a more efficient stripping, and

a truer indication of the stripping action on a larger scale operation. Also, the total quantity of strip solution was varied somewhat so that the effect of more or less strip solution might be studied at the same time.

The experiments were begun as before, activating six samples of fresh gel at 300°C, and determining moisture, heat of wetting and purifying capacity of the gel by the methods described in Appendix D. The cycles of adsorption loading and stripping proceeded as before. Three replicate adsorption determinations of each gel sample were made, and the quantity of acid strip solution was varied among the three determinations. The quantities of acid used were 1/6, 1/4, and 1/3 gallon per pound of gel in the first strip (1.5, 2.25, and 3.0 milliliters per gram of gel, respectively). The second strip was 1.5 milliliter per gram of gel in each case. Thus the total quantities of strip used on the three replicate determinations corresponded to 1/3, 5/12, and 1/2 gallon per pound of gel, respectively.

The results of the five adsorption cycles using two acid strips are summarized in Tables 14 through 18, respectively. The three determinations for each gel sample are listed in the order of acid strip quantity used (strip I). The gel samples are listed in the order of moisture analyses as before. The data on adsorption,

Table 14. Adsorption Tests on Silica Gel with Two Sulfuric Acid Strips, Cycle 1.

% H_2O	ΔH_w cal. g.gel	Strip I ml. g.gel	Product solution at 7 days x_P g.ox. ml.	R_P	v_P ml. g.gel	Prod.oxide $x_P v_P$ g.ox. g.gel	MeOH wash g.oxides g. gel	H_2SO_4 Strip g.oxides g.gel	R_G	$K_o=\frac{R_G}{R_P}$	S_H	Material Balance Error %
		1.5	0.147	0.83	1.81	0.266	0.081	0.140	8.8	10.6	4.67	-1.03
3.33	28.4	2.25	0.146	0.80	1.81	0.264	0.090	0.149	8.6	10.8	4.90	+ 2.23
		3.0	0.147	0.79	1.83	0.269	0.081	0.163	8.5	10.8	4.85	+ 4.26
		1.5	0.148	0.82	1.77	0.262	0.083	0.124	8.7	10.6	4.81	-4.68
3.42	28.3	2.25	0.145	0.85	1.73	0.251	0.074	0.147	8.6	10.1	4.84	-4.06
		3.0	0.146	0.84	1.76	0.260	0.081	0.124	8.7	10.4	4.82	-5.50
		1.5	0.145	0.84	1.75	0.254	0.083	0.148	7.8	9.3	4.88	-1.42
3.50	29.8	2.25	0.147	0.88	1.78	0.262	0.075	0.173	7.4	8.4	4.50	+ 3.66
		3.0	0.148	0.83	1.80	0.266	0.070	0.174	7.5	9.0	4.67	-1.83
		1.5	0.142	0.79	1.68	0.238	0.074	0.172	7.4	9.4	5.48	-1.62
3.95	28.6	2.25	0.143	0.75	1.70	0.243	0.074	0.164	7.5	10.0	5.65	-2.24
		3.0	0.147	0.78	1.71	0.251	0.075	0.154	7.8	10.0	5.27	-2.44
		1.5	0.144	0.83	1.81	0.261	0.072	0.157	7.7	9.3	4.77	-0.41
3.96	27.5	2.25	0.144	0.83	1.82	0.262	0.072	0.156	8.0	9.6	4.75	-0.41
		3.0	0.143	0.84	1.81	0.259	0.073	0.163	7.6	9.0	4.75	+ 0.61
		1.5	0.165	0.74	1.70	0.280	0.088	0.144	7.3	9.9	5.30	-3.03
4.17	33.2	2.25	0.157	0.78	1.70	0.270	0.080	0.175	7.2	9.2	5.33	-0.57
		3.0	0.159	0.73	1.73	0.275	0.070	0.198	7.0	9.5	5.54	+ 2.84

Notes: Feed Solution: x_F = 0.164 g. oxide/ml., R_F = 2.1 Hf/Zr x100, v_F = 3.0 ml./g. gel (tests 1-5)

x_F = 0.176 g. oxide/ml., R_F = 2.1 Hf/Zr x 100, v_F = 3.0 ml./g. gel (test 6)

Strip II = 1.5 ml./g. gel

Table 15. Adsorption Tests on Silica Gel with Two Sulfuric Acid Strips, Cycle 2.*

% H_2O	ΔH_w cal. g.gel	Strip I ml. g.gel	Product solution at 7 days x_P g.ox. ml.	R_P	v_P ml. g.gel	Prod.oxide $x_P v_P$ g.ox. g.gel	MeOH wash g.oxides g.gel	H_2SO_4 Strip g. oxides g. gel	R_G	$K_G = \frac{R_G}{R_P}$	S_H	Material Balance Error, %
		1.5	0.145	0.91	1.85	0.268	0.083	0.145	7.1	7.8	4.22	+0.81
3.00	26.5	2.25	0.147	0.86	1.85	0.272	0.080	0.150	7.4	8.6	4.42	+2.03
		3.0	0.140	0.91	1.85	0.259	0.082	0.166	6.9	7.6	4.38	+3.05
		1.5	0.142	0.88	1.82	0.258	0.085	0.130	7.6	8.6	4.54	-3.86
3.33	30.0	2.25	0.146	0.88	1.82	0.266	0.080	0.133	7.5	8.5	4.41	-2.44
		3.0	0.146	0.91	1.82	0.266	0.090	0.118	7.4	8.1	4.26	-3.66
		1.5	0.146	1.0	1.88	0.274	0.080	0.144	6.6	6.6	3.76	+1.22
3.45	25.1	2.25	0.143	0.99	1.90	0.272	0.081	0.136	7.0	7.0	3.88	-0.61
		3.0	0.146	1.0	1.87	0.273	0.079	0.159	6.7	6.7	3.78	+3.86
		1.5	0.144	1.1	2.00	0.288	0.049	0.174	6.4	5.8	3.28	+3.87
3.74	25.5	2.25	0.144	1.1	2.04	0.294	0.054	0.155	6.9	6.3	3.20	+2.24
		3.0	0.144	0.97	2.00	0.288	0.057	0.156	7.1	7.3	3.80	-1.83
		1.5	0.145	0.83	1.90	0.275	0.060	0.150	7.1	8.6	4.70	-1.42
3.97	27.0	2.25	0.144	0.85	1.90	0.273	0.063	0.144	6.8	8.1	4.45	-2.44
		3.0	0.144	0.86	1.88	0.271	0.061	0.150	7.1	8.2	4.44	-2.03

Notes: Feed Solution: $x_F = 0.164$ g. oxide/ml.
$R_F = 2.1$ Hf/Zr x 100
$v_F = 3.0$ ml./g. gel

Strip II = 1.5 ml./g.

*The previous six samples were condensed to five samples to make them large enough.

Table 16. Adsorption Tests on Silica Gel with Two Sulfuric Acid Strips, Cycle 3.

% H_2O	ΔH_w cal./g.gel	Strip I ml./g.gel	Product solution at 7 days x_P g.ox./ml.	R_P	V_P ml./g.gel	Prod.oxide $x_P v_P$ g.ox./g.gel	MeOH wash g. oxides/g. gel	H_2SO_4 Strip g.oxides/g. gel	$K_o = \frac{R_G}{R_P}$	S_H	Material Balance Error, %	
		1.5	0.144	0.93	1.85	0.266	0.082	0.130	6.5	7.0	4.20	-3.66
3.20	28.9	2.25	0.144	0.86	1.90	0.274	0.065	0.156	6.3	7.3	4.40	+0.61
		3.0	0.144	0.88	1.88	0.271	0.068	0.155	6.3	7.2	4.35	+0.41
		1.5	0.147	0.86	1.88	0.276	0.060	0.135	7.4	8.6	4.35	-4.26
3.23	27.1	2.25	0.143	0.87	1.88	0.269	0.061	0.144	6.6	7.6	4.44	-3.66
		3.0	0.143	0.94	1.85	0.264	0.080	0.119	7.3	7.8	4.20	-5.89
		1.5	0.145	0.89	1.82	0.264	0.072	0.152	6.8	7.7	4.42	-0.81
3.40	29.0	2.25	0.145	0.85	1.83	0.265	0.072	0.148	6.5	7.7	4.60	-1.42
		3.0	0.147	0.95	1.80	0.264	0.075	0.161	6.2	6.5	4.12	-1.63
		1.5	0.142	0.85	1.84	0.261	0.082	0.142	6.5	7.7	4.65	-1.22
3.68	27.8	2.25	0.143	0.83	1.84	0.263	0.083	0.139	6.7	8.1	4.75	-1.42
		3.0	0.143	0.83	1.84	0.263	0.083	0.139	6.7	8.1	4.75	-1.42
		1.5	0.145	0.91	1.95	0.283	0.062	0.125	7.5	8.3	4.00	-4.48
3.73	24.5	2.25	0.148	0.90	1.94	0.287	0.060	0.119	7.0	7.8	4.02	-5.29
		3.0	0.146	0.91	1.94	0.283	0.061	—	-	-	4.00	—

Notes: Feed Solution: x_F = 0.164 g. oxide/ml.
R_F = 2.1 Hf/Zr x 100
v_F = 3.0 ml./g. gel

Strip II = 1.5 ml./g. gel

(—) Data unavailable due to loss of stripped oxide sample.

Table 17. Adsorption Tests on Silica Gel with Two Sulfuric Acid Strips, Cycle 4.

% H_2O	ΔH_w cal. g.gel	Strip I ml. g.gel	Product solution at 7 days x_P g.ox. ml.	R_P	v_P ml. g.gel	Prod.oxide $x_P v_P$ g.ox. g.gel	MeOH wash g. oxides g. gel	H_2SO_4 Strip g. oxides g. gel	R_G	$K=\frac{R_G}{R_P}$	S_H	Material Balance Error, %
		1.5	0.124	0.96	2.12	0.263	0.041	0.150	5.9	6.2	3.66	+ 3.65
3.36	29.0	2.25	0.123	0.95	2.12	0.261	0.041	0.150	6.2	6.5	3.74	+ 3.19
		3.0	0.125	1.0	2.10	0.262	0.049	0.163	5.5	5.5	3.52	+ 8.21
		1.5	0.128	1.1	2.16	0.276	0.059	0.115	6.7	6.1	3.02	+2.74
3.44	26.5	2.25	0.128	1.0	2.12	0.271	0.054	0.128	6.3	6.3	3.40	+3.42
		3.0	0.128	1.0	2.16	0.276	0.066	0.102	6.4	6.4	3.33	+1.37
		1.5	0.128	1.0	2.15	0.275	0.055	0.136	6.5	6.5	3.36	+7.30
3.82	25.7	2.25	0.126	1.0	2.14	0.269	0.047	0.153	6.0	6.0	3.42	+7.07
		3.0	0.126	1.0	2.14	0.269	0.051	0.159	6.0	6.0	3.42	+8.66
		1.5	0.125	0.96	2.02	0.252	0.050	0.148	5.6	5.9	3.80	+2.74
3.82	25.7	2.25	0.125	0.96	2.00	0.250	0.048	0.169	5.6	5.9	3.84	+6.62
		3.0	0.124	0.96	2.04	0.253	0.055	0.124	6.3	6.6	3.86	-1.37
		1.5	0.124	0.97	1.89	0.234	0.060	0.124	5.9	6.1	4.05	-4.55
4.26	30.0	2.25	0.123	0.93	1.91	0.235	0.068	0.150	5.6	6.0	4.23	+4.55
		3.0	0.126	0.93	1.92	0.247	0.045	0.169	5.6	6.0	4.10	+4.10

Notes: Feed Solution: x_F = 0.146 g. oxide/ml.
R_P = 2.1 Hf/Zr x 100
v_F = 3.0 ml./g. gel

Strip II = 1.5 ml./g. gel

Table 18. Adsorption Tests on Silica Gel with Two Sulfuric Acid Strips, Cycle 5.*

% H_2O	ΔH_w cal./g.gel	Strip I ml./g.gel	Production solution at 7 days x_P g.ox./ml.	R_P	v_P ml./g.gel	Prod. oxide $x_P v_P$ g.ox./g.gel	MeOH wash g. oxides/g. gel	H_2SO_4 Strip g. oxides/g.gel	R_G	$K=\frac{R_G}{R_P}$	S_H	Material Balance Error, %
3.42	26.1	1.5	0.122	1.1	2.16	0.263	0.045	0.139	6.0	5.5		3.17 + 2.05
		2.25	0.123	1.1	2.16	0.266	0.050	0.121	6.0	5.5		3.16 0
		3.0	0.123	1.1	2.12	0.261	0.049	0.145	5.9	5.4		3.21 +3.88
3.59	25.8	1.5	0.126	1.1	2.20	0.277	0.030	0.148	5.3	4.8		3.02 +3.88
		2.25	0.126	1.1	2.24	0.282	0.036	0.122	5.8	5.3		2.96 + 0.45
		3.0	0.126	1.1	2.19	0.276	0.030	0.149	5.5	5.1		3.03 +3.88
3.65	26.8	1.5	0.124	1.0	2.18	0.270	0.033	0.125	5.8	5.8		3.42 -2.24
		2.25	0.124	1.1	2.20	0.273	0.030	0.144	5.7	5.2		3.06 +2.05
		3.0	0.123	1.1	2.20	0.270	0.030	0.146	5.4	4.9		3.10 +1.82
3.74	27.1	1.5	0.123	1.1	2.21	0.272	0.026	0.155	5.7	5.2		3.09 +3.42
		2.25	0.123	1.0	2.20	0.270	0.026	0.155	5.6	5.6		3.41 +2.96
		3.0	0.125	1.0	2.24	0.280	0.042	0.127	5.6	5.6		3.28 +2.51

Notes: Feed Solutions: x_F = 0.146 g. oxide/ml.
R_F = 2.1 Hf/Zr x 100
v_F = 3.0 ml./g. gel

Strip II = 1.5 ml./g. gel

*The previous five samples were condensed to four samples to make them large enough.

product oxide, and oxide weights in the methanol wash and sulfuric acid strip are given together, with the oxide balance error calculated as before for each adsorption run.

The weight of oxide given for the sulfuric acid strip was the total of the two strips for each determination. It was found that the second stripping generally contained from ten to fifteen percent of the total weight obtained, with no consistent relationship between the amount of strip solution used in strip I and the adsorbate removed by each of the two strips. The hafnium was analyzed in each strip sample, and was found to be higher in strip II than in strip I in every case. Average values of Hf/Zr x 100 were obtained (for the total strip) and these are presented as R_G in the data.

Difficulty in obtaining reproducible stripping results was still evident from an examination of the data, even though two separate strips were used. Moreover, there was no consistent relationship between the quantity of strip used and the amount of stripped oxide obtained. Of the 25 sample tests made over the five cycles, 14 tests showed the highest ratio to strip the most material from the gel, 6 tests indicated the middle ratio to be the most effective, and in 4 tests the lowest ratio was actually found to strip the most oxide. One test was indeterminate

owing to the loss of one of the stripped oxide samples. These apparent anomalies indicate that the difficulty may lie in the comparatively small size of gel samples used in the tests. Small samples would show up errors in washing and stripping more so than would larger samples, as in a pilot plant test.

Values of the hafnium adsorption factor S_H indicated generally better reproducibility in this series of tests than in the series made previously. There was closer agreement in values of R_p (product hafnium analyses) obtained from the three determinations of adsorptive capacity made on each gel sample, which may indicate that the spectrographic analysis method for hafnium was improved over that used in the previous series of analyses. Since it was fairly well established that R_p was the main variable in question entering the calculation of S_H, it would be expected that better agreement in product hafnium analyses would result in better agreement of S_H values.

The values of the oxide material balance error showed an almost equal distribution between negative and positive values, with the very few large positive values occurring in the runs where an unusually large figure for stripped oxide was obtained. In the first three cycles a majority of runs (33 out of 47) showed negative material balance errors, while in the last two cycles a majority of runs

(23 out of 27) showed positive material balance errors. This trend could be explained as due to residual oxide in the first three cycles causing a negative error, with a partial stripping of some of this residual oxide in the last two cycles causing a positive error. This is not too plausible an explanation, however, since the adsorption factor S_H continued to decline the last two cycles. It is more likely that some error was entering the oxide determinations, particularly the stripped oxide, which gave a high figure in some of the experiments.

The hafnium separation factor K_0 was calculated for each adsorption experiment as the ratio $\frac{R_G}{R_P}$, the ratio of the Hf/Zr x 100 on the gel to that in the product at equilibrium. Giffen (7) found that the separation factor should be a constant (near 14) for normal gel, and presumed that a decrease would indicate deleterious changes in the gel causing the purifying capacity to be reduced. The values obtained in the present work ranged from about 10 in cycle 1 to about 5 in cycle 5. The starting gel was thus somewhat lower in K_0 than the statistical average of 13.18, which Giffen found from Baer's experimental values ranging from 8 to 20. The starting gel may therefore not have been quite as active as the average tested by Baer, so that a K_0 lower than his average would have resulted.

Also, if the hafnium analyses in the high range (R_C) had been a little low, low values for K_0 would also have been found.

If the separation factor K_0 could be used as satisfactorily as the hafnium adsorption factor S_H to determine the purifying capacity of the gel, K_0 would have the advantage of applying to any adsorption test, without requiring the weighing of the gel sample or measuring the feed solution. A sample of product solution would be required for analysis, and the gel would be methanol-washed and stripped with sulfuric acid to obtain the hafnium-zirconium adsorbate. Determination of the separation factor would then require only accurate Hf/Zr x 100 analyses of oxide stripped from the gel and oxide in the product solution.

In Figure 4 the separation factor K_0 is plotted against the hafnium adsorption factor S_H. If the graph is extended to the origin of its axes, i.e., where there is zero preferential adsorption and K_0 and S_H would both be 1.0, a straight-line curve may be drawn through the points to obtain a fair correlation. It was observed that, if the oxide balance error were used as a criterion of the validity of individual points in Figure 4, those runs having an error of 4 percent or greater would generally fall the fartherest from the line extrapolated from the

Figure 4. Relation Between Zirconium Purification Factors.

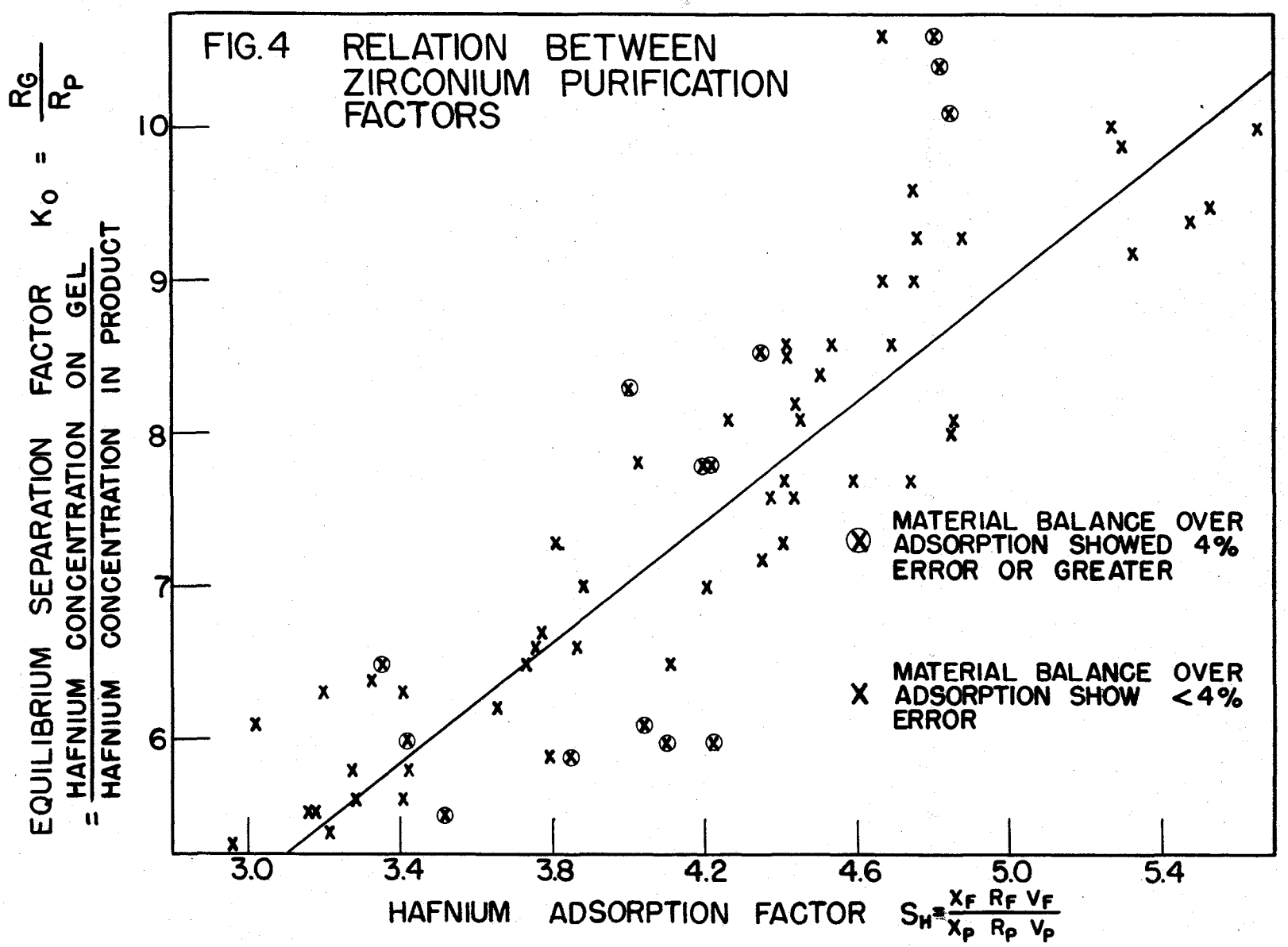
FIG. 4 RELATION BETWEEN ZIRCONIUM PURIFICATION FACTORS
EQUILIBRIUM SEPARATION FACTOR $K_o = \frac{R_G}{R_P}$ = HAFNIUM CONCENTRATION ON GEL / HAFNIUM CONCENTRATION IN PRODUCT
10
9
8
7
6
3.0
3.4
3.8
4.2
4.6
5.0
5.4
HAFNIUM ADSORPTION FACTOR $S_H = \frac{X_F R_F V_F}{X_P R_P V_P}$
MATERIAL BALANCE OVER ADSORPTION SHOWED 4% ERROR OR GREATER
MATERIAL BALANCE OVER ADSORPTION SHOW <4% ERROR

origin. By using the division of 4 percent error rather arbitrarily, many of the most scattered points could be rejected and the correlation improved somewhat.

Of the total of 74 determinations plotted, 17 were rejected on the basis of oxide balance error, which is about 20 percent of the total number of points. Three of the rejected points fell close enough to the curve to have been otherwise considered valid. Rejection of the points on the basis of high material balance error appeared to give a satisfactory analysis of the adsorption data for the correlation in Figure 4.

Figure 4 shows that, allowing for the difficulty in obtaining reproducible results in S_H and K_0, a reasonably good correlation can be obtained between S_H and K_0. It would thus appear that the separation factor K_0 could be used as well as S_H to determine purifying capacity of gel. Moreover, the feed solution properties would not have to be known as in the determination of S_H. As Giffen indicated, a change in K_0 (corresponding to a change in S_H) shows a change in the chemical nature of silica gel and a reduction in its capacity for purifying the zirconium solution.

The values of S_H obtained in each cycle of gel testing were plotted against the respective cycle number in Figure 5. An arithmetic average value was calculated and

Figure 5. Purification Factors Over Five Adsorption Cycle Gel Stripped Twice After Each Cycle.

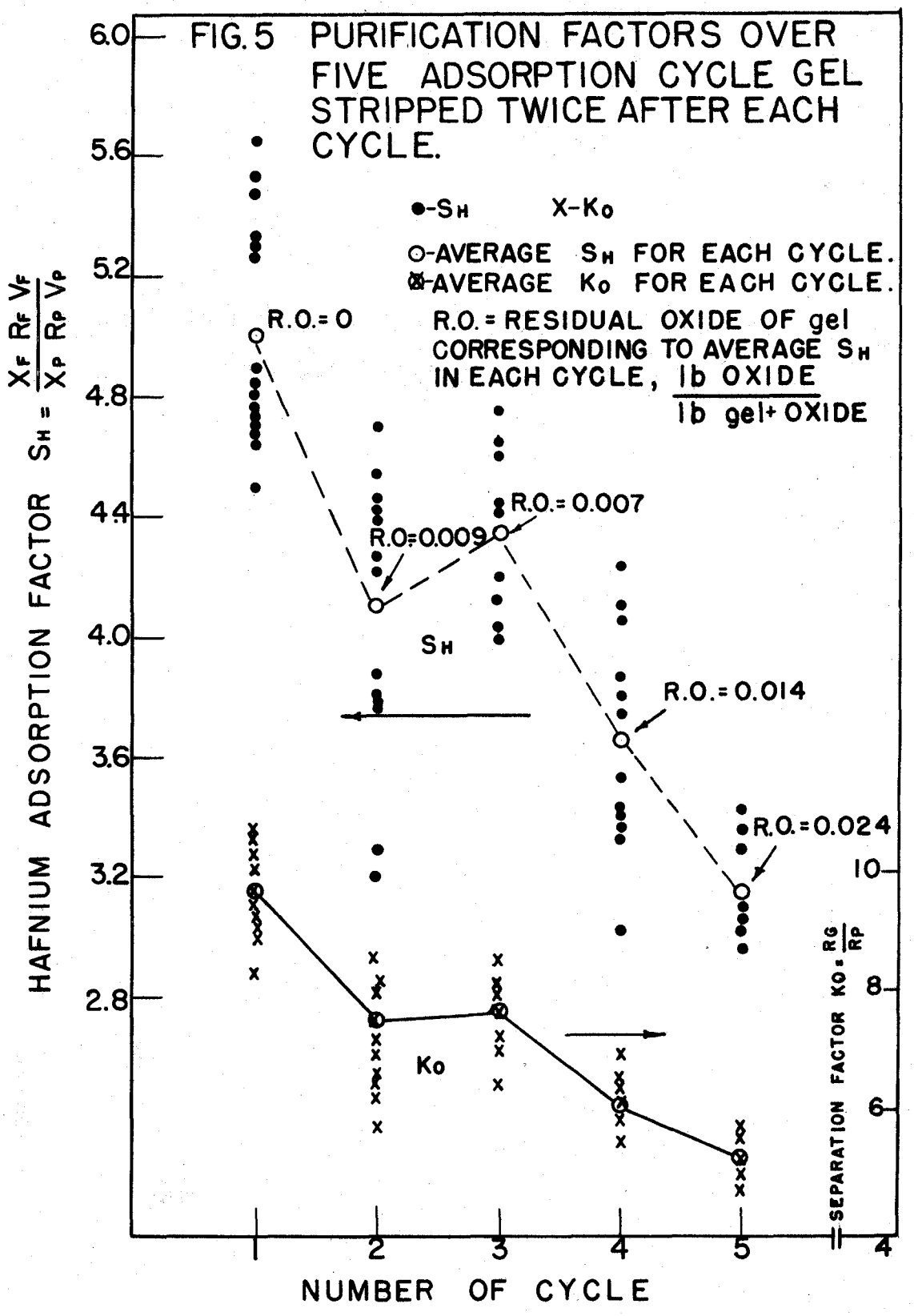
FIG. 5 PURIFICATION FACTORS OVER FIVE ADSORPTION CYCLE GEL STRIPPED TWICE AFTER EACH CYCLE.
●-SH X-Ko
○-AVERAGE SH FOR EACH CYCLE.
⊗-AVERAGE Ko FOR EACH CYCLE.
R.O. = RESIDUAL OXIDE OF gel CORRESPONDING TO AVERAGE SH IN EACH CYCLE, lb OXIDE / lb gel+ OXIDE
R.O.= 0
R.O.= 0.007
R.O.=0.009
R.O.= 0.014
R.O.= 0.024
SH
Ko
HAFNIUM ADSORPTION FACTOR SH = XF RF VF / XP RP VP
SEPARATION FACTOR KO = RG/RP
NUMBER OF CYCLE
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
10
8
6
4
1
2
3
4
5

plotted for each cycle, and a straight-line curve drawn through the average points to show the change in average S_H over the cycles tested. The graph shows that the decrease in average hafnium adsorption factor was about 40 percent over the five cycles tested. Comparing this graph with Figure 3, which showed the average adsorption factor decrease for the previous series of tests to be about 60 percent, the indication is that using two separate sulfuric acid strips and a little more strip solution helped to maintain the gel in better condition.

The values of residual oxide from Figure 2 corresponding to the average S_H values in Figure 5 have been noted thereon, and it is seen that the residual oxide increased from 0.009 gram per gram of gel after cycle 2 to 0.023 gram per gram of gel after the fifth cycle. These results indicated a much more satisfactory condition of the gel at the end of five cycles of adsorption and stripping, using two separate strips, than was in evidence from the previous experiment where only one strip was used (Figure 3).

Also shown on Figure 5 are the values of the separation factor K_0 found in each cycle over which the gel was tested. An arithmetic average value was calculated for each cycle and the average points were connected with a straight line. The general shape of the graph is

similar to that for the adsorption factor S_H as would be predicted from the correlation in Figure 4. The average value of K_0 decreased from about 9.7 for the initial cycle to about 5.3 for the fifth cycle. Giffen's value of 13.18 for K_0 was an average established from 40 experimental values ranging from 8 to 20, so that a value of 8 to 13 could be considered as the lower range of values possible for normal gel. After the initial cycle the values of K_0 were found to definitely decrease out of the range of the "normal" values.

The results obtained from the small-scale preliminary loading and stripping determinations show that the gel should be stripped on a larger scale to obtain a more definite picture of the applicability of the stripping operation. The small-scale determinations showed that reclaimed gel could be compared with fresh gel by relatively simple analytical procedures, and these procedures can be used to estimate the purifying capacity of an unknown reclaimed gel in any actual operation.

D. Experimental Pilot Plant Gel Treatment

Demonstration of the treatment process on a scale considerably larger than that used so far was important to confirm the laboratory findings summarized at the end

of the last section. The applicability of the process to any larger scale of operation will depend upon factors which are of little importance in small-scale experimentation. Among these is the importance of the physical characterisitics of the gel on the processing.

For the pilot plant experimentation, spent gel from the continuous column operated by Giffen (7) was drained thoroughly of occluded solution by means of suction through an aspirator. The drained "process gel" was used to determine the weight of "process gel" to activated gel, so that the actual weight of activated gel being processed would be known from the weight of drained gel. This weight ratio was found to be near 1.6, so that 1.6 pounds of thoroughly drained gel would produce 1 pound of activated gel.

Figure 6 is an overall flow diagram of the proposed gel treatment process. Spent gel from the storage tank at the bottom of the column was drained as a slurry into an open 20-gallon glass-lined tank fitted with a diaphragm valve and water-pump aspirator. After drawing off all occluded solution the spent gel was treated batchwise in turn with pure methanol, 7N sulfuric acid, and pure water, each solution being thoroughly drained off by suction before addition of the next.

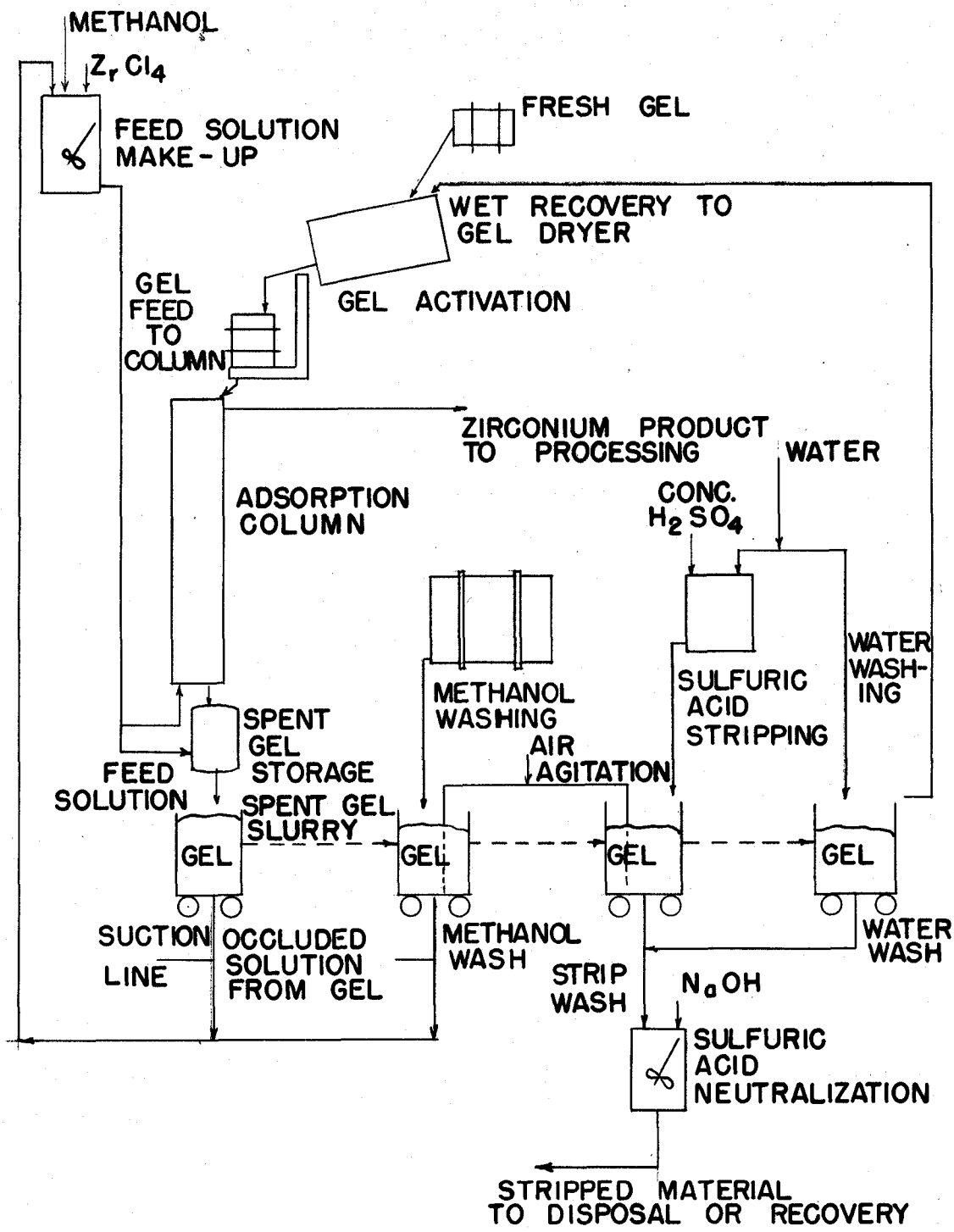

FIG. 6 FLOW DIAGRAM OF SILICA GEL RECOVERY PROCESS

The sulfuric acid strip solution was made up to 7N standard by adding one volume of the concentrated acid (36 N) to four volumes of pure water in a glass-lined open tank. The maximum temperature attained was found to be about 75°C, so that on any large scale operation water-cooling would have to be provided for this operation. While the strip solution was cooling, methanol was added to the drained gel and was allowed to remain in contact with it for about one hour.

In the methanol washing the gel was found to be very difficult to mix with a stirrer of any kind, and a 3/4 inch plastic rod actually broke in attempting to use it to attain agitation. The tank was therefore covered with a wooden lid, and a vigorous air agitation was used. The air was supplied from the compressed air lines (a moisture trap was used) and was fed into the gel-methanol slurry from above through a half-inch plastic tube. The tube was moved from time to time, since the mixing it supplied was not very extensive in the gel bed. The methanol wash solution was removed by suction, and the gel was treated with the sulfuric acid strip. Air agitation was used, with a contact of about two hours being allowed, and the strip solution was removed by suction.

Air agitation would not be too satisfactory on a very large scale of gel treatment. However, a sufficiently

powerful stirrer at low speed (about 30 rpm.) would give enough agitation to insure uniform contacting of gel with the wash and strip solutions. A glass-lined tank with agitator would be ideal for this, such as Jacobs (10) used for his uniform loading test.

The stripped gel was washed with pure water until the effluent gave a negative test for Hf-Zr with ammonia, and was 0.01N sulfuric acid or less. In the water-washing no agitation was used, the water being drawn through the gel bed continuously by suction. After removal of all the wash water the gel was removed from the tank, and was activated at 250-300°C for 24 hours in an automatically controlled gas-fired tray drier. No air-drying was necessary, for, although the gel is easier to handle if it is free-flowing, this was not important in this case. The activated gel was then put through the continuous column for its first recycle (second cycle) and this spent gel was then recovered as before.

Seven batches or treatments of spent gel were run in all, representing gel processed from cycles 1, 2 and 3. The gel from cycle 1 was processed in three batches of about equal size, to give a total amount of gel sufficient for a continuous column run. Of the three batches, two were duplicate runs with respect to the stripping, with 0.27 and 0.28 gallon of strip per pound of activated gel

being used. In the third run 0.17 gallon per pound of activated gel was used. The three batches were water-washed, activated, and run through the continuous column separately for cycle 2. The batches were then recovered separately from the cycle 2 as spent gel.

The gel from cycle 2 was processed in two batches, the quantity of sulfuric acid strip being varied as before. After the methanol washing, which was kept as constant as possible in all the batch treatments, the respective gel batches were treated with the same quantity of strip solution as had been used in the previous processing. Only two batches were run because some of the gel was in doubt as to how it had been treated (the previous cycle). The gel batches were processed separately through the activation as before.

For cycle 3 the gel batches were treated in batchwise contact with feed solution in a 20-gallon glass-lined tank to obtain spent gel for the third reprocessing. The gel was not put through the continuous column in this cycle because the column was no longer in operation. The spent gel batches were stripped as before, and their processing completed.

In Table 19 the results of these treatments are summarized. The weight of gel in each batch is given as its activated weight, which was used as the basis of the

Table 19. Pilot Plant Gel Treatment.

Test	Gel processed, activ. lb.	Methanol wash: Gal. MeOH / lb. gel	Methanol wash: lb. oxide wash / lb. gel	Sulfuric acid strip: Gal. strip / lb. gel	Sulfuric acid strip: lb. oxide / lb. gel	Water wash: Gal. water / lb. gel	lb. resid. oxide / lb. gel + oxide
Cycle 1-A	55	0.29	0.044	0.27	0.107	0.31	0.0012
1-B	54	0.30	0.044	0.28	0.105	0.37	0.0014
1-C	58	0.28	0.045	0.17	0.103	0.26	0.0066
Cycle 2-A	40	0.25	0.052	0.25	0.102	0.30	0.0027
2-B	51	0.29	0.057	0.19	0.102	0.27	0.0114
Cycle 3-A	39	0.26	0.054	0.26	0.102	0.33	0.0065
3-B	50	0.30	0.046	0.20	0.104	0.30	0.0121

quantities of solution used. The methanol wash used was kept fairly constant, from 0.25 to 0.30 gallon per pound of gel. The high ratio of sulfuric acid strip was 0.25 to 0.28 gallon per pound of gel, and the low ratio of strip was 0.17 to 0.20 gallon per pound of gel. There was found to be no appreciable difference in the quantity of oxide stripped per pound of gel over the three cycles of test, so that the effect of the difference in quantity of strip solution was not apparent from this standpoint.

The residual oxide was determined for each batch of gel at the end of the processing in each cycle, to ascertain the degree of completeness of the stripping. Residual oxide was determined by treating a sample of the gel with hydrofluoric acid, as described in Appendix D. The values of residual oxide are given in the last column of Table 19. With the higher strip ratio, residual oxide was found to be 0.0012 to 0.0014 gram oxide per gram of gel after the initial cycle, and was 0.0065 gram per gram of gel after the third cycle. Using the lower strip ratio, the residual oxide was considerably higher; it was found to be 0.0066 gram per gram of gel after the initial cycle and 0.0121 gram per gram of gel after the third cycle.

From these data it appears that the gel will process much better using about 0.3 gallon strip solution per pound of gel than a lower ratio such as was tried in these

experiments. The recovered gel from the third cycle having the low residual oxide content was tested in 7-day batch contact adsorption, and was found to have a hafnium adsorption factor of 4.65. Comparing this with the adsorption factor found for fresh gel, averages being 5.44 and 5.20 from Figures 3 and 5, the gel from the large-scale recovery is seen to have a relatively high purifying capacity at the end of three cycles. It would appear feasible to use it for at least four cycles, therefore, and the gel could probably be used more. The K_0 was found to be 11.6 at the end of three cycles, higher than the average 9.7 for fresh gel shown in Figure 5.

A standard screen analysis was made on the activated reclaimed gel to compare it with fresh gel, to show how much of the gel was broken down mechanically in going through the gel feeder, column and recovery process. A weighed sample of gel was tested by hand-shaking and a similar sample was run for comparison on a mechanical shaker. The material on each screen was weighed and computed as percent of the starting sample. A sample of fresh gel was run on the mechanical shaker as a control.

The screen analyses are given in Table 20. The amount of gel broken down to finer than 200 mesh does not exceed about 2.3 percent of the total, so the mechanical degradation of the gel cannot be said to be very serious.

The pilot plant stripping treatments on spent gel showed that satisfactory stripping could be obtained over three treatment cycles on the same gel, using a quantity of 0.25 to 0.28 gallon of strip solution per pound of gel.

Table 20. Standard Screen Analyses of Reclaimed and Fresh Gels.

Retained on mesh	Reclaimed gel Percent by hand	Reclaimed gel Percent by shaker	Fresh gel Percent by shaker
28	1.0	1.0	1.0
35	18.0	19.5	18.1
48	34.3	34.0	36.5
65	19.5	19.3	14.6
100	14.1	14.3	17.3
200	10.0	9.0	10.8
-200	2.3	2.3	0
Loss	0.8	0.6	1.7
	100.0	100.0	100.0

The gel was found to compare favorably with fresh gel in the hafnium adsorption factor obtained by batch contact adsorption testing. Mechanical degradation of the reclaimed gel was found to be insignificant.

V. DISCUSSION AND CONCLUSIONS

A. Analysis of Data and Results

For an overall evaluation of the experimental work on gel recovery, it would be desirable to compare the major results obtained in the pilot plant gel treatment with the results of the small-scale experiments. Such a comparison would give a more comprehensive picture of the gel recovery than would a stepwise evaluation of each set of results. Individual results can be evaluated for their individual worth, of course, but comparison with other results is more meaningful.

The small-scale work was performed, first, to determine the quantities of materials required for the gel processing, and secondly, to study the change in purifying capacity of reclaimed gel obtained with the proposed treatment. The pilot plant work was performed to simulate a larger scale gel recovery, utilizing the methods evolved in the laboratory experiments.

The quantities of materials for washing and stripping estimated in the laboratory work were found to give consistent results in the pilot plant gel treatment. In the laboratory tests the quantity of methanol (Table 2) found to give good washing was 0.22 to 0.25 gallon per pound of gel, and in the pilot plant work (Table 19) 0.25 to 0.30

gallon of methanol per pound of gel produced good washing results. While the amount of oxide washed off varied from 0.044 to 0.057 pound oxide per pound of gel, subject to the completeness of drainage of occluded material, the oxide stripped after the washing varied only from 0.107 to 0.102 pound oxide per pound of gel. The pilot plant washing results therefore appear to have been consistent. Using gentle agitation, such as low-speed stirring in a glass-lined kettle, good methanol washing would be obtained using 0.25 gallon per pound of gel.

The acidified methanol strip was omitted from the processing. Analysis of Jacobs' work showed (Run 5 in Table 1) that when hafnium-saturated gel was first washed with methanol, little or no material was obtained by acidified methanol stripping which would be low enough in hafnium concentration to merit recycling through the adsorption column. Run 5 showed that such stripping of gel saturated with respect to hafnium would give only stripped material higher in hafnium concentration than the feed solution used with the gel. If such stripped material were incorporated as feed solution by neutralization of the acidified methanol, the build-up of hafnium would nullify any small advantage of increasing the zirconium yield through acidified methanol stripping.

Stripping of washed gel on a laboratory scale did not provide very definite results (Table 4) due to the variation in the adsorbate content of the gel tested. It appeared that the quantity of strip solution required would be between 0.15 and 0.43 gallon per pound of gel. In the pilot plant gel processing (Table 19) 0.25 to 0.28 gallon of strip per pound of gel was used to obtain gel with a very minute quantity of unstripped material remaining after each cycle of adsorption and stripping. From the pilot plant results it would appear that using about 0.3 gallon of strip per pound of gel should produce sufficiently complete stripping to enable the gel to be re-used in the adsorption system. Less acid was found to leave a considerably greater amount of material behind on the gel.

It is important to note that the quantity of oxide stripped in the pilot plant runs was fairly consistent, 0.107 to 0.102 pound of oxide per pound of gel, while throughout the small-scale work the stripped material varied to some extent in quantity, so that it was difficult to obtain reproducible stripping results. This variation was noted in Tables 2, 4, 7, and 9 through 18, where stripping was performed on small gel samples. It was believed that stripping large samples of gel served to eliminate or average out such variations apparently

inherent in the determinations with small samples. From this standpoint the larger scale stripping tests had the greatest value in demonstrating satisfactory stripping without excessive variation in results.

The stripped gel was water-washed to remove occluded acid after drainage. Small-scale determinations were made first to determine approximately how much water would be required for complete removal. In Table 5, material balance showed that drainage and water-washing removed 99-plus percent of the acid charged as strip solution. The amount of water estimated to be required was 0.3 to 0.4 gallon per pound of gel. In the pilot plant work the gel was washed continuously with water until the effluent wash was acid-free, and 0.26 to 0.37 gallon per pound of gel gave thorough washing. The variability in water requirements can probably be ascribed to differences in completeness of drainage of the occluded acid. Average water requirements would be about 0.31 gallon per pound of gel, based on an average of the values shown in Table 19.

The final step in the regeneration process consisted of heating the washed gel at 300°C to restore its adsorptive capacity. In the heating the moisture content was reduced to about 3.5% by weight (wet basis) which was found to correspond to the maximum heat of wetting of the

gel (Figure 1). Over-activation or heating at too high a temperature was found to permanently reduce the heat of wetting, and thus reduce the adsorptive capacity of the gel in the adsorption process.

Evaluation of regenerated gel in a large-scale adsorption operation could best be made by three determinations, as follows:

1. Residual oxide (Appendix E);
2. heat of wetting (Appendix F);
3. moisture content (Appendix F).

The residual oxide would serve as a control on the stripping process. A high residual oxide, i.e., 0.0075 gram per gram of gel or more, would eliminate poorly stripped gel from re-use in the adsorption process, and would demonstrate the necessity of using more strip solution on the next batch of gel. A low residual oxide, however, would not necessarily mean that such gel would give satisfactory results in the adsorption process. Satisfactorily stripped gel may not be activated properly, so that a test must be made of the activation.

The heat of wetting was found to be about 34 calories per gram of gel for activated gel (Figure 1) at the maximum. A gel with a heat of wetting of 30 calories per gram or more would be considered satisfactory from the standpoint of activation. A gel having a low residual oxide

in combination with a high heat of wetting could be put through the adsorption process with considerable confidence. A low heat of wetting, however, might be due either to incomplete activation or to over-activation. In either case the gel would not be satisfactory for reuse in the adsorption process even if the residual oxide were very low. To determine whether a low heat of wetting would be caused by under- or over-activation, the moisture content of the gel should be found.

The moisture content corresponding to the maximum heat of wetting was shown to be about 3.5% (Figure 1). A gel with an appreciably higher moisture should be reactivated and the heat of wetting and moisture determined again. If the heat of wetting continued to be low the gel should be discarded as it would probably give poor results in the adsorption process. A low moisture content, i.e., 3% or less, would itself signify gel that had been over-activated. The heat of wetting in such a case would also be low, and such gel should be discarded.

In a large-scale operation the temperature of activation could be readily controlled in either a tray drier, or rotary drier, and thereby eliminate a possible source of difficulty in the activation. If the stripping of the spent gel were thorough, and the activation carefully controlled, there should be no regenerated gel rejected

as unsatisfactory.

The three recommended determinations would provide the maximum information in evaluation of regenerated gel, with a minimum of time requiredin analytical work. Each determination would be of only limited value by itself, but the combination would give a definite comparison with fresh gel in three independent criteria.

The only single criterion that could be used to evaluate the gel would be its hafnium adsorptive capacity, which could be obtained only by a 7-day adsorption test. This determination would have the obvious disadvantage of requiring a large inventory of regenerated gel to be carried during the period of the adsorption test. More important, perhaps, the adsorption test would not show the cause of a poor adsorptive capacity, as would the residual oxide, heat of wetting and moisture determinations. Adsorptive capacity would be dependent upon each of these three factors, and the adsorption test would give no information as to whether the stripping or the activation was at fault.

Related to the gel regeneration and evaluation was the matter of zirconium lost in the stripping of the gel. The silica gel was found to adsorb considerable zirconium along with the hafnium, and the strip solution removed this zirconium in a form in which it could not be recycled through the adsorption purification process. The adsorbed

zirconium, therefore, constituted a net loss in the adsorption. The zirconium loss could be related to the total zirconium put through the adsorption cycle if the operating conditions for the adsorption are known.

The most important condition involved in the adsorption would be the ratio of the weight of gel used to the quantity of product solution. This ratio may be designated as W/P as defined by Giffen (7) in his plant design, where W is the pounds of gel and P the gallons of product solution through the continuous adsorption column in a given time period. Some latitude is permissible in choosing W/P for a given plant design, Although a ratio of about 2.0 was recommended by Giffen. For the sake of comparison, it would be convenient to assume W/P values of 1.5, 2.0, 3.0, and 4.0 pounds of gel per gallon of solution, and calculate the zirconium loss that would result if a specified feed solution were used.

The feed solution specified by Hansen had a total concentration of 23% tetrachlorides by weight dissolved in pure methanol, the solute having a Hf/Zr x 100 of 2.5. This feed contained the equivalent of (approximately) 1.0 pound of oxides per gallon, of which 0.025 pound would be hafnium oxide and 0.975 pound would be zirconium oxide. It may be considered that all the hafnium will be adsorbed by the gel, since the hafnium must be reduced from about

25,000 parts per million to about 100 parts per million to produce specification zirconium.

In the experimental work the silica gel was found to adsorb an equivalent of about 0.1 pound of oxides per pound of gel. The continuous adsorption column would operate under steady-state conditions, so that a simple material balance could be used to evaluate zirconium loss for a given amount of silica gel being used. For example, if a W/P of 2.0 were used, 2 pounds of gel would adsorb about 0.2 pound of oxides of the 1.0 pound of oxides per gallon of solution. The adsorbate would contain 0.025 pound of hafnium oxide, and the other 0.175 pound would be zirconium oxide. Zirconium adsorbed and therefore lost in the stripping process would be 0.175 pound out of 0.975 pound put through, or 18.0 percent loss. The above calculation can be simplified for any W/P by the following equation:

$$\text{Percent Zr loss} = \frac{(W/P)(0.1) - 0.025}{0.975} (100) .$$

In Table 21 the computed values of zirconium loss are given for each assumed value of W/P. From these data it appears that the minimum zirconium loss would be about 10 percent, using the theoretical minimum quantity of gel, 1.19 pounds per gallon of solution. Giffen (7) computed this quantity to be required with an adsorption column of

infinite length, in which case the column would operate under equilibrium conditions. Using 1.5 to 2.0 pounds of gel per gallon of solution, zirconium loss would be 13 to 18 percent, which approximates Giffen's estimate of 85 percent zirconium yield for his plant design.

Table 21. Zirconium Lost in Stripping of Spent Gel. (Feed: 2.5 in Hf/Zr x 100).

$\frac{W}{P}$ $\frac{\text{Lb. gel}}{\text{Gal. soln.}}$	Zirconium loss, percent of throughout	R_G Hf/Zr x 100 of adsorbate
1.19	9.6	30.5
1.5	12.8	22.9
2.0	18.0	16.3
3.0	28.2	10.4
4.0	38.5	7.6

The composition of the adsorbate was readily calculated for each of the assumed values of W/P. Using W/P of 2.0, for example, the adsorbate would consist of 0.025 pound of hafnium oxide to 0.175 pound of zirconium oxide. The HfO_2/ZrO_2 x 100 would therefore be 14.3. Converting this value to Hf/Zr x 100 by the third equation in appendix B, the adsorbate analysis would be 14.3/0.874 or

16.3 in Hf/Zr x 100. The calculations to obtain the Hf/Zr x 100 can be simplified by using the equation:

$$\text{Adsorbate Hf/Zr x 100} = \frac{0.025}{(W/P)(0.1) - 0.025}\left(\frac{100}{0.874}\right).$$

The adsorbate hafnium concentration R_G was found to decrease with increase in the quantity of gel used. Such a decrease would be expected because the hafnium must distribute itself over larger amounts of gel, while the gel will adsorb a constant amount of zirconium and hafnium. When more gel is used the additional zirconium adsorption will decrease the hafnium concentration of the adsorbate as well as increase the zirconium loss.

For the minimum quantity of gel, 1.19 pounds of gel per gallon of solution, the computed adsorbate analysis would be 30.5 in Hf/Zr x 100. In such a column operation, equilibrium would be attained between solution and gel, so that the equilibrium separation factor could be calculated. The separation factor is the ratio of the hafnium concentration in the adsorbate to the hafnium concentration in the solution in equilibrium with the gel. The solution in equilibrium with gel would be the feed solution just entering the bottom of the column, meeting the gel passing downward out of the column (note column in Figure 6). The calculated separation factor would therefore be 30.5 divided by 2.5, or 12.2, which compares well with the value

of 13.18 which Giffen (7) found by statistical analysis of 40 small-scale experimental results.

The calculated values of adsorbate Hf/Zr x 100 (Table 21) were observed to vary uniquely with W/P and with the calculated zirconium loss for steady-state conditions assumed in the calculations. In large-scale continuous column operations the adsorbate hafnium analysis could therefore be used as a criterion of zirconium loss. Material stripped from the spent gel would merely have to be analyzed spectrographically to obtain its Hf/Zr x 100. The values in Table 21 could be used for column operations using the specified feed of 2.5 in Hf/Zr x 100. With a different feed the relationship between zirconium loss and adsorbate hafnium concentration would be altered, but the relationship would be unique for a given feed Hf/Zr x 100. If the feed were changed, the zirconium losses and adsorbate hafnium concentration could be readily re-calculated using the equations given above. The new hafnium analysis would then be substituted for 0.025 in the equations.

B. Cost Analysis and Comparison

In the cost estimate which Beyer and Giffen (3) made over the semi-works plant to produce 1000 pounds of zirconium per month, they concluded that purified zirconium

could be produced by the adsorption process for $7.60 per pound as the purified salt $ZrOCl_2.8H_2O$. Compared with this was the estimated cost of 10.14 per pound by the Y-12 process involving solvent extraction (7). Since the completion of Giffen's work, revisions in the cost of the Y-12 process (14, 15), as well as the present investigation on silica gel, have indicated the need for a re-evaluation of the cost comparison.

Of primary consideration in a cost estimate of the adsorption process is the question of whether or not the gel recovery is economical. Millard and Maitland (13) have made an economic evaluation of the gel recovery process, and have incorporated the cost analysis into a cost comparison between the Y-12 and adsorption processes.

The requirements in chemicals and utilities for gel processing are summarized in Table 22. The sulfuric acid and caustic soda for the strip solution neutralization were readily calculated from the fact that 0.3 gallon of 7N sulfuric acid strip was required per pound of gel. The fuel and electricity requirements are calculated from the manufacturer's data on a suitable rotary drier such as might be used for the activation of the silica gel.[1]

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[1] A pilot plant study of this type drier was made by R. B. Edwards of the Ames Laboratory.

The total reclamation chemical costs are approximately $0.05 per pound of gel compared to $0.44 per pound of new gel.

From the cost figures for new and reclaimed gel the cost of gel per pound of zirconium produced, as a function of the number of cycles the gel may be used, is summarized in Table 23. This cost analysis shows that the cost of gel will vary with the number of times the gel is recycled through the adsorption process. If an amount of gel equal to 2.0 pounds per gallon of solution is assumed from Giffen's work, 2.22 pounds of gel is required per pound of zirconium. The more the gel is recycled, the smaller will be the proportion of comparatively expensive fresh gel required. Table 23 shows that the greatest gel cost reduction occurs in the first 2 or 3 re-cycles, after which the reduction is quite modest. It appears that, from an economic standpoint, 4 or 5 cycles of gel use would be the most that would ever be worth while.

The total cost comparison between the Y-12 process, as reported by Ramsey and Whitson (14, 15), and the adsorption process, is given in Table 24. These cost figures indicate that the silica gel adsorption process is not competitive with the Y-12 extraction process. The overall cost by the adsorption process is $7.10 per pound of zirconium, which includes gel recovery, while the

Table 22. Cost of Silica Gel Reclamation.
(Basis: 1 lb. silica gel.)

Item	Amount required	Unit cost	Cost lb. gel
Sulfuric acid	1.02 lb.	$0.02	$0.020
Caustic soda	0.84 lb.	0.03	0.025
Fuel (natural gas)	0.0048 MCF	0.75	0.004
Electricity	0.120 KWH	0.04	0.005
			$0.054

Table 23. Economy of Silica Gel Recovery.
(Based on silica gel cost of $0.44 per pound.)

No. of cycles	Lb. fresh gel Lb. Zr	Lb. rec. gel Lb. Zr	Individual gel costs: Fresh gel Lb. Zr	Used gel Lb. Zr	Total gel Lb. Zr
1	2.22	0	$ 0.975	$ 0.000	$ 0.975
2	1.11	1.11	0.488	0.060	0.548
3	0.74	1.48	0.325	0.080	0.405
4	0.56	1.66	0.244	0.090	0.334
5	0.44	1.78	0.195	0.096	0.281
6	0.37	1.85	0.163	0.100	0.263
7	0.32	1.90	0.139	0.102	0.241

overall cost by the Y-12 process is $5.37 per pound of zirconium.

Table 24. Comparative Cost of Producing Purified Zirconium.

(Basis: 1 lb. zirconium as purified compound).

Item	Y-12: ZrO_2[a]	Adsorption: $ZrOCl_2 \cdot 8H_2O$
Raw materials and chemicals	2.85[b]	1.88[c]
Plant amortization (5-year)	0.40	1.17[d]
Power and utilities	0.09	0.25[d]
Direct labor and supervision	0.44	1.90[d]
Overhead	1.59	1.90[d,e]
	$5.37	$7.10

[a]From Y-12, based on period July 1950 through April 1951. Ramsey and Whitson (14).

[b]From $1.12 to $1.25 of this cost is salicylic acid. Replacement of this precipitant with ammonium phthalate, which is largely recoverable, should reduce this cost.

[c]Includes silica gel with 5-cycle life assumed. Millard and Maitland (13).

[d]Beyer and Giffen estimate (3).

[e]Taken as 100 percent of direct labor on the usual Ames Laboratory basis.

In comparing the cost of the adsorption process with gel recovery and without gel recovery, the cost of using more fresh gel would have to be balanced against the plant cost with gel recovery. In Table 24 the raw materials and chemicals item includes silica gel at $0.29 per pound of zirconium, an assumption of 5-cycle gel life. If fresh gel were used with no gel recovery, Table 23 shows the cost would be $0.98 per pound of zirconium, or $0.69 more than the figure c in Table 24. To compensate for this higher cost of fresh gel, the plant cost without gel recovery would have to be reduced by at least $0.69. Such a reduction would mean reducing Giffen's overall plant cost estimation of $1.17 by more than 50 percent. It is unlikely that the equipment for the gel recovery would amount to over 15 percent of the total plant installation cost, so that the gel recovery would be definitely profitable.

The comparison of the Y-12 extraction process with the adsorption process in Table 24 was made on the basis of actual plant operation for the Y-12 process, while some phases of the adsorption process cost estimate were based purely on estimates. The report by Millard and Maitland (11) presents a discussion of the estimations in the process costs and the possible cost reductions that could be

made in both the Y-12 process and the adsorption purification process.

It can only be concluded, from the rather uncertain economic picture obtained from the above cost comparison, that the adsorption purification process with gel reclamation would be more costly than the Y-12 process currently in use at Oak Ridge. It is likely that more extensive pilot plant work with the adsorption process would show economies possible which would make it more nearly competitive with the Y-12 process. The latter, however, has the advantage in being in operation with the cost of zirconium purification relatively well established.

C. Conclusions and Recommendations

This investigation was not an exhaustive one in that the conditions of gel testing were necessarily limited to those of comparison of the recovered gel with fresh gel, the fresh gel being the basis established previously for an analysis of the adsorption process. The study of the spent gel produced the following conclusions relating to the gel recovery and to the recovered gel:

1. Methanol-washing of the drained spent gel from the adsorption column was found to remove at least 20 percent of the total material occluded and adsorbed on the gel. The wash contained

low-hafnium material that could be recycled for further purification.

2. A single agitated batch-contact washing with methanol was found preferable to a more prolonged continuous washing. An excessive use of methanol should be avoided. Satisfactory washing was obtained with about 0.25 gallon of methanol per pound of gel.
3. Stripping the washed gel with acidified methanol solution did not strip enough material suitable for recycle to be economical. The gel was stripped most satisfactorily with 7N aqueous sulfuric acid following the methanol washing.
4. Pilot plant stripping treatments on spent gel showed that satisfactory stripping could be obtained over three treatment cycles on the same gel, using a qunatity of 0.25 to 0.28 gallon of strip solution per pound of gel. The gel was found to resemble fresh gel in its zirconium purifying capacity in actual adsorption testing. The mechanical degradation of the reclaimed gel was insignificant.
5. Water-washing of the stripped gel was found to satisfactorily remove the acid strip, with 0.33 to 0.37 gallon per pound of gel being sufficient

to wash. The gel could then be activated at 300°C to normal moisture content, about 3.5% on the wet basis.

6. The quantity of unstripped adsorbate as residual oxide on the reclaimed gel was correlated with the hafnium adsorptive capacity of the gel. Hafnium adsorptive capacity was measured by controlled batchwise adsorption tests on samples of reclaimed gel, and it was found that hafnium was adsorbed to the greatest degree when the residual material on the gel was a minimum.
7. The total adsorptive capacity of the gel was found to decrease very slightly, while hafnium adsorptive capacity decreased considerably, due to the residual oxide on reclaimed gel. The gel lost its capacity to purify much sooner than it lost its total adsorptive capacity.
8. Evaluation of regenerated gel in a large-scale adsorption operation could best be made by determining its residual oxide, heat of wetting, and moisture content. The residual oxide would provide a control on the stripping operation, while the heat of wetting and moisture analyses would show whether or not the gel had been activated properly.

9. In the sulfuric acid stripping of the gel, zirconium adsorbed along withhafnium was effectively lost because zirconium could not be readily reclaimed from the strip solution. This zirconium loss was calculated as about 13 to 18 percent in column operation using 1.5 to 2.0 pounds of gel per gallon of solution. The use of more gel would increase the zirconium adsorbed and lost through stripping.

10. In a large-scale continuous column operation, the adsorbate hafnium analysis could be used as a criterion of zirconium loss becaue the adsorbate hafnium concentration and zirconium loss are uniquely related in a steady-state adsorption using a given feed.

11. The cost of gel reclamation was found to be about $0.05 per pound of gel, compared to $0.44 per pound for new gel. The major reduction in the overall cost of zirconium through gel recovery was found to be in the first three or four reuses, beyond which gel recovery would not materially influence the cost of zirconium purification.

12. An estimation for a semi-works plant producing 1000 pounds of zirconium per month by the

adsorption process showed the overall cost to be $7.10 per pound of zirconium, including gel reclamation. In comparison, the overall cost established by actual operation of the Y-12 solvent extraction process in current use was found to be $5.37, or less, per pound of zirconium.

Any future work on the adsorption purification process would involve mainly the actual production of purified zirconium. Zirconium production would be based on further study to improve the operation of the continuous column, and further development of the gel reclamation process and its incorporation into the purification process to give a smoothly-operating production unit.

The factors to be determined in gel recovery should include the following:

1. A careful analysis should be made of the labor requirements and overhead, especially a study of whether additional labor would be required for gel recovery other than that required for the adsorption column operation alone. Labor requirements could not intelligently be estimated from the previous pilot plant work, and the approximation made by Giffen was a considerable part of the overall cost of purified zirconium (Table 24).

2. The possibility of recovering the material stripped from the gel, and applying it to hafnium concentration, should be studied.
3. The possibility of utilizing reclaimed gel after the third or fourth cycle, after it has outlived its usefulness in the zirconium purification process, should be considered. The gel might well be used in gas-drying or similar applications, since the investigation indicated that its total adsorptive capacity (heat of wetting) might not diminish appreciably although its hafnium adsorptive capacity might be reduced considerably.

The use of the recalimed gel in the adsorption process would entail essentially a comparison with fresh gel in performance, utilizing the analytical procedures recommended in Conclusion 8 to evaluate the regenerated gel in the adsorption column could be ascertained by establishing a zirconium material balance in continuous column runs, and computing the zirconium yield with fresh and reclaimed gels. Reclaimed gel giving appreciably lower yield for a given purification would be discarded. Calculation of material balances from the experimental runs would also enable corroboration of the method for calculating the zirconium loss recommended in Conclusion 10.

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VIII. APPENDIX: ANALYTICAL PROCEDURES

A. Determination of Solute as Oxide from Solution Samples

The solutions that were sampled for hafnium determination and total oxide content included the sulfuric acid strip, and methanol-tetrachloride feed, product, and wash solutions. Samples were pipetted to 0.01 milliliter, usual sample being about 2 milliliters. Aqueous ammonia was added to the solution to precipitate the hafnium-zirconium hydroxides. In the case of the methanol feed solution the sample was diluted with water first to prevent too violent a reaction.

The gelatinous precipitate of hydroxides was filtered on coarse analytical filter paper, washed with distilled water, and dried at low heat overnight in a weighed porcelain crucible. Ignition to the oxides at 700°C was then performed in an electric muffle, after which the samples were cooled in a dessicator. The oxide samples were weighed to 0.001 gram and sent to the Spectrographic Laboratory for hafnium analysis.

B. Hafnium Analysis of Oxide Samples

The hafnium concentration as reported by the Spectrographic Laboratory was the weight ratio of hafnium to

zirconium in the oxide sample, Hf/Zr x 100. Because it would sometimes be desired to express the concentration of hafnium in some other way, the following conversions can be made:

$$\% \text{ Hf} = \frac{(\text{Hf/Zr x } 100)\ 100}{100 + (\text{Hf/Zr x } 100)}$$

where % Hf is the weight percent hafnium of the total of hafnium and zirconium in the oxide sample;

$$\% \text{ HfO}_2 = \frac{(\text{Hf/Zr x } 100)\ 87.4}{100 + 0.874(\text{Hr/Zr x } 100)}$$

where $\%HfO_2$ is the weight percent of hafnium oxide in the oxide sample. The factor 0.874 is the conversion factor for changing Hf/Zr to the corresponding oxide ratio, based on the ratio of molecular weights. Thus it can be shown that

$$HfO_2/ZrO_2 \text{ x } 100 = 0.874(\text{Hf/Zr x } 100).$$

C. Titrations of Water Washings from The Stripped Gel.

Three liters of 0.54 N NaOH solution were made up for acid titrations by dissolving Baker Reagent Grade NaOH pellets in distilled water, dissolving thoroughly, and allowing the solution to stand overnight in a tightly stoppered Pyrex glass flask. The solution was standardized

by titration with primary standard potassium acid phthalate, which was accurately weighed and dissolved in a little distilled water. Methyl red was used as indicator, and the titration was completed when the indicator was just colorless. The NaOH solution was used over a considerable period, and its normality was checked from time to time.

The acid wash solution to be titrated was sampled by pipetting 1 to 5 milliliters accurately to 0.01 milliliter. The size of the solution sample was influenced by the strength of the solution being determined, in order to obtain consistent accuracy for all the titrations. Titration was complete at the same end-point as that used in the standardization. In calculation of total acidity in each wash solution, normality was multiplied by the total volume of the solution in milliliters to give total milliequivalents.

D. Testing of Silica Gel.

In the various studies of gel behavior in which initially fresh gel was used, the following determinations and procedures were used:

1. Gel preparation

Fresh gel was taken from the drum as supplied by Davidson Chemical Corporation, Baltimore, Maryland, the

samples being 200 to 250 grams in size. The normal or "as-received" moisture content of this gel was about 5%; depending upon the moisture content and degree of activity desired in the various samples, heating was employed for 10 minutes to an hour or longer in an electric muffle at 250 to 300°C. A flat quartz tray was found suitable for purpose as it allowed uniform activation of the gel sample.

Slight alteration of this procedure enabled gel to be prepared with abnormally high or low moisture content for special studies. If it was desired that the gel have a lower moisture content and activity than normal, it was "sintered" or heated at a temperature of 600 to 700°C. If a high moisture content was wanted, distilled water was added to the gel sample taken from the drum. The gel was thoroughly mixed and allowed to stand 2 to 3 days to insure uniform distribution of the moisture throughout the gel.

All prepared gel samples were placed in stoppered flasks and allowed to stand a short time, to cool if they had been heated, and thoroughly mixed by hand-shaking to insure uniformity. A ten-gram portion was poured quickly into a weighed weighing-bottle having a ground-glass stopper. Total weight was obtained to 0.001 gram and about one-third of this gel was then poured quickly into a clean 00 crucible. This was ignited at 800°C for 18

to 24 hours to determine moisture content. The remaining two-thirds of the gel was reweighed and this gel was used to determine heat of wetting. Subtracting this weight from the previous weighing gave the weight of the moisture sample.

2. Moisture determination

The ignited moisture samples were cooled in a dessicator just long enough to be able to handle them. If they were allowed to stand longer it was found that even the ignited gel would pick up a small amount of moisture. The gel was poured into a small weighed weigh-bottle having a ground-glass stopper, and weighed. This weight of ignited gel was subtracted from the original "wet" weight to give ignition loss, and dividing the loss by the original gel weight gave the percent moisture on the "wet" basis.

3. Heat of wetting determination

A calibrated thermos-type calorimeter with an electric stirrer and thermometer was used to determine the calorific value of heat of wetting of the gel, using distilled water to wet the gel. The weighed gel sample was poured into the clean dry calorimeter, the stopper was replaced, and the stirrer was started. A powerstat transformer, type 1126, was used to control the stirring speed at about 250 rpm. After 2 to 3 minutes a practically constant

temperature was attained in the calorimeter as shown by the thermometer, the bulb of which was adjusted to just touch the gel in the bottom of the calorimeter. A 25 milliliter sample of distilled water was pipetted from a flask and run into the calorimeter. After 3 to 4 minutes a constant final temperature was attained in the calorimeter.

The following data were recorded and calculations made therefrom:

Gel weight; specific heat of gel = 0.22

Initial gel temperature = t_g

Initial water temperature = t_w

Final temperature = t_f

Calorimetric weight equivalent = 24.3 grams

Water weight = 25 grams

Total calorimetric weight = 24.3 + (0.22)(gel weight)

$$\text{Initial average temperature} = \frac{(\text{total cal. wt.})t_g + 25t_w}{\text{total cal. wt.} + 25} = t_1$$

Then $\Delta t = t_f - t_1$

$$\text{Hence, heat of wetting} = \frac{(\text{total cal. wt.} + 25)\Delta t}{\text{gel weight}} = \Delta H_w \ .$$

The moisture and heat of wetting were each determined three times on each gel sample tested, to obtain reproducible results, and an arithmetic average taken of the three values.

4. Adsorption testing of gel

Except in the case of the adsorption tests on loaded gel (Table 7), batch contact adsorption tests were performed on three replicate gel portions of about equal size for each gel sample studied. In starting each sample, 25 to 30 grams of gel was taken so that by the end of the fourth or fifth cycle the samples would still be large enough for testing. The gel samples were weighed accurately and fresh feed solution of known oxides content and Hf/Zr x 100 was measured out, 3 milliliters per gram of gel being used. It was found better to add the gel to the solution in a flask, as this minimized the exposure of the gel to the air. The flask was then tightly stoppered, and was shaken from time to time to insure uniformity of the system.

If 1-hour determinations of the adsorption were desired, the time of the contacting of the gel and solution was recorded, whereas if only the 7-day adsorption was being determined the time was not so important. At the end of the time period desired, a 2 to 3 milliliter sample of the effluent product solution was carefully pipetted from the flask, and this solution sample was processed to obtain the solute as oxide by the method described in Appendix A. Weight of oxide in the effluent sample was reported as concentration in grams per milliliter of solution.

The samples of oxide were sent to the Spectrographic Laboratory for determination of the hafnium as Hf/Zr x 100.

5. Stripping of Gel

At the termination of the adsorption test the loaded gel was freed of product effluent solution by suction of the gel slurry on a Buchner funnel. The volume of the product solution was measured in a graduate cylinder. This volume was divided by the grams of gel used in the adsorption test, so the product volume was reported as milliliters per grams of gel.

The gel was then washed with a volume of pure methanol equal to the volume of the feed solution used. Most effective washing was attained by using the methanol in several small portions, allowing each to run completely through the gel before adding the next portion. The total methanol washing was then neutralized with ammonia to precipitate the solute as hydroxide, which was filtered, washed with water, ignited to oxide, and weighed as such. The methanol-washed oxide was reported as grams per gram of gel.

The washed gel samples were replaced in their respective flasks and 7N aqueous sulfuric acid was added to each sample. The amount of acid used was 3 milliliters per gram of gel, in some cases some fraction of this where two strips in sequence were to be used. A contact time

of 2 hours between strip and gel was allowed. Frequent shaking was used to help maintain good contact between gel and solution.

The strip solution was removed by filtering the slurry on a Buchner funnel, and the gel cake was then washed with water. About 3 milliliters of water per gram of gel was generally required to obtain a good washing in most cases. A plastic bottle fitted with a siphon was used to give a continuous washing after the flask containing the gel-acid slurry was thoroughly rinsed. The washed gel was then ready for reactivation for the next adsorption cycle. In some cases the gel was stripped with a second portion of acid strip after air-drying the washed gel overnight. This stripping was performed exactly as the first.

The combined solution and washings from each gel sample stripping were neutralized with ammonia to precipitate the solute as hydroxide. This hydroxide was filtered on a Buchner funnel using coarse analytical filter paper, was water-washed, dried at low heat overnight, ignited to oxide and weighed as such to 0.001 gram. The stripped oxide was reported as grams per gram of gel. The samples of oxide were sent to the Spectrographic Laboratory for determination of hafnium as Hf/Zr x 100.

E. Direct Determination of Residual Oxides on the Gel

A normally activated sample of reclaimed gel to be determined, 5 to 10 grams weighed to 0.001 gram, was placed in a polyethylene beaker. Aqueous hydrofluoric acid (40%) was measured out in a plastic graduate cylinder, allowing 5 milliliters per gfam of gel. The gel was covered with an equal volume of distilled water to prevent too violent a reaction when the acid was added. CAUTION: This should be performed in a hood. The gel was allowed to dissolve completely and the beaker was placed on very low heat overnight. The top of an electric muffle covered with a sheet of asbestos, the muffle being used at about 500°C, was found convenient for this purpose. Too much heat, even the "low" of a hotplate, would cause melting of the plastic beakers.

Overnight evaporation of the hydrofluoric acid-silica solution removed silica as the volatile tetrafluoride according to the reaction

$$SiO_2 + 4\ HF \longrightarrow SiF_4 + 2\ H_2O$$

and the residue remaining consisted of hafnium-zirconium tetrafluorides. This residue readily dissolved in water, and ammonia was added to the resulting solution to precipitate the solute hydroxides. The precipitate was

filtered, washed with water, ignited to oxide and weighed as such to 0.001 gram. The residual oxide was reported as grams per gram of total or loaded gel.

F. "Improved" Methods for Determination of Moisture and Heat of Wetting

In the moisture and heat of wetting determinations, some difficulty was had in obtaining reproducible results. It was thought that some of the trouble might be due to exposure of gel samples to the air in transferring them prior to the final determinations. Therefore, some of the procedures described in Appendix D were modified slightly.

1. Moisture determination

The ignited and cooled moisture samples were retained in their crucibles, and the crucibles were placed in small weighed weighing-bottles, instead of pouring the gel into the weighing-bottles. The total weight was obtained for the gel and crucible, and the gel was then removed and the crucible weighed alone in the weighing-bottle. The difference gave the weight of the ignited gel, and subtracting this from the original "wet" gel weight gave the loss due to moisture. Dividing the loss by the original weight gave the percentage of moisture.

2. Heat of wetting determination

The weighed gel sample was not poured into the calorimeter, but was retained in the weigh-bottle and this bottle (without the stopper) was placed in the calorimeter. The specific heat of Pyrex glass is 0.22 calories per gram per °C, which was multiplied by the weight of the bottle. The resulting quantity was added to the calorimetric weight equivalent. The only other change in the calculations was that 50 milliliters of water was used to wet the gel instead of 25 milliliters, to prevent too high an initial temperature rise when the water was added to the gel in the weigh-bottle.

The procedure used was otherwise the same, the thermometer and stirrer being adjusted so that they extended into the gel. The stirrer was started and a constant initial temperature obtained before adding the water. A constant final temperature was obtained after the wetting.

G. Experimental Comparison of "Standard" and "Improved" Analytical Methods

To compare the reproducibility of moisture and heat of wetting results obtainable with the analytical procedures described in Appendices E and F, three replicate determinations each of moisture and heat of wetting were

were made on one of the fresh gel samples activated normally. The "standard"and "improved" methods were each used on the same sample of gel.

Table A summarizes the results of these determinations. The data are arranged in each column to show the spread in values obtained. By both methods a maximum variability of about 10 percent was obtained for moisture, and the average values were about the same for each, being 3.66% and 3.63% by the standard and improved methods, respectively.

Table A. Analytical Methods for Moisture and Heat of Wetting.

	"Standard" Method		"Improved" Method	
	% H_2O	ΔH_w, cal./g.	% H_2O	ΔH_w, cal./g.
	3.80	35.0	3.80	32.6
	3.73	31.7	3.65	31.8
	3.45	30.5	3.45	31.0
Av.	3.66	31.1	3.63	31.8

Variability of results for heat of wetting was considerably less by both methods than for moisture determination. If the value of 35.0 obtained by the standard method were rejected as out of line with the other values, the range was 3.8 percent, and the range by the improved method was 4.9 percent. The average values for heat of wetting were

31.1 and 31.8 calories per gram of gel by the standard and improved methods, respectively.

The conclusion from this study is that the improved methods give little better results, if any, over the standard techniques in analysis of moisture and heat of wetting. It is difficult to explain the comparatively large variability in moisture content, but it is not too important since in any event the heat of wetting would be the more significant index of the two in checking activation of a gel sample.